Electronic Supplementary Information

Metal Free Direct C(sp2)-H Arylaminations Using Nitrosoarenes to 2-hydroxy-di(het)aryl Amines as Multifunctional Aβ-aggregation Modulators

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Experimental:

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. Dichloromethane (CH_2Cl_2) was freshly distilled from phosphorus (V) oxide (P_2O_5). Commercial grade xylene, benzene and toluene were distilled over CaH_2 before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. ^1H, ^{13}C NMR spectroscopy: *Varian Mercury plus 400 MHz, Bruker 600 MHz* (at 298 K). Chemical shifts, δ (in ppm), are reported relative to TMS δ (^1H) 0.0 ppm, δ (^{13}C) 0.0 ppm) which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^1H) 7.26 ppm, δ (^{13}C) 77.2 ppm; CD_3OD, (^1H) 3.31 ppm, δ (^{13}C) 49.0 ppm) were used for calibration. Column chromatography: Merck or Spectrochem silica gel 60-120 under gravity. IR: spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in *m/z* (% of basis peak). FETEM measurements of the samples were carried out in a JEOL (JEM 2100F) microscope with an operating voltage of 200 kV. Nitrosoarene derivatives[i] and 4-methyl-5-phenylcyclohexane-1,3-dione[ii] were synthesized by literature procedures.

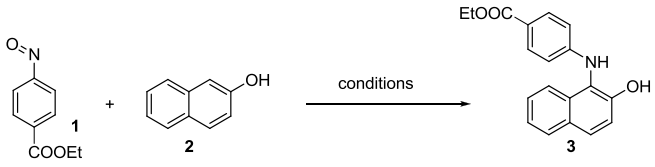
ThT Assay for fibrillation kinetics:

Stock solution of Amyloid β-40 was prepared in de-ionised water, aliquots of this solution were then lyophilized and stored at -20°C. For each experiment Amyloid β- 40 (Aβ-40) peptide concentrations were normalized to 1μM by further dilution using 20 mM Phosphate buffer saline (PBS) and a final concentration of 20 μM Thioflavin T (ThT) was added in a NEST 96-well plate along with 50 μM of the respective molecules in each well. This plate was then sealed using an opti-seal to prevent evaporation. The fibrillation kinetics were followed using a BioTek Synergy H1 fluorescence plate reader at an excitation wavelength of 440 nm and an emission wavelength of 490 nm. Readings were recorded in triplicate every 40 min for a period of 20 h. The amyloid fibrillation growth rates were calculated by fitting the initial portion of the aggregation kinetics using the equation $y = A + B*\exp(-kx)$.

Transmission Electron Microscopy

10 μL of sample solution was added on to a carbon coated copper grid and this was left for 2 minutes, it was later wicked off with a filter paper. The grid was then rinsed with deionized water and a 5 μL 4% uranyl acetate replacement (EMS) droplet was placed on to the grid. After a minutes this solution was wicked off and the grid was air dried. The imaging was performed on JEOL (JEM 2100F) microscope with an operating voltage of 200 kV.

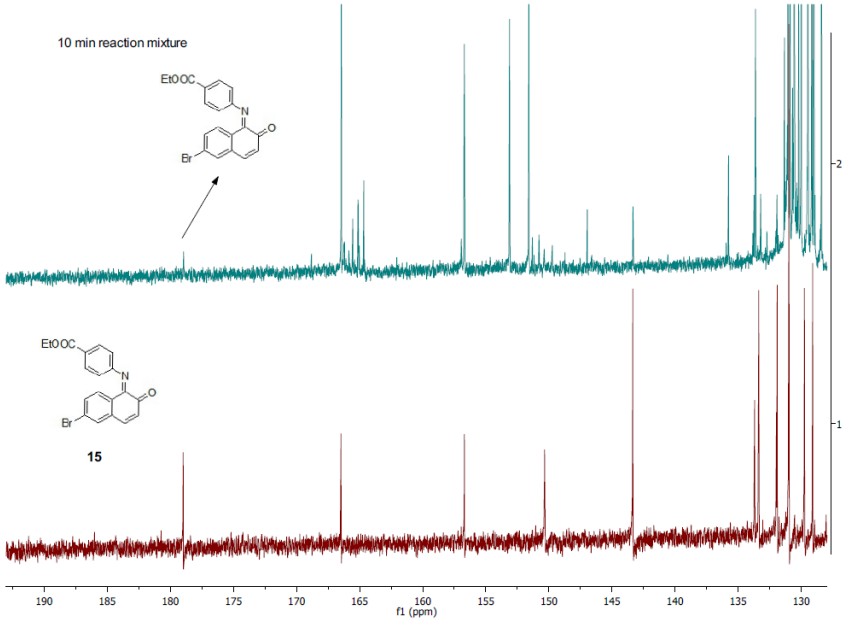
Table s1: Optimization of reaction conditions



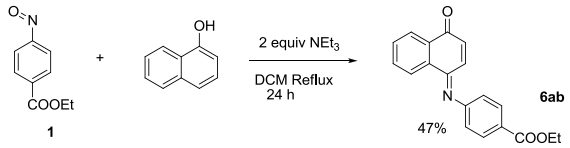
entry	conditions	isolated yield (%)
1[b]	NEt_3(2), DCM, 40 ˚C	48
2[c]	NEt_3(2), DCM, 40 ˚C	64
3[d]	NEt_3(2), DCM, 40 ˚C	76
4	NEt_3(2), DCM, 40 ˚C	85
5	NEt_3(2), DCM, rt	75
6	DCM, 40 ˚C	46
7	K^{t}OBu, DCM, 40 ˚C	30
8	NEt_3(2), Toluene, 40 ˚C	79
9	ipr_2NEt (2), DCM, 40 ˚C	64
10	NEt_3 (2), DCE, 80 ˚C	53
11	K_2CO_3 (2), DCM, 40 ˚C	36
12	NEt_3 (2), MeOH, 40 ˚C	69
13	NEt_3 (2), EtOH, 40 ˚C	45
14	THIQ, DCM, 40 ˚C	22

[a]All reactions were performed with of 2-naphthol (0.17 mmol), nitrosobenzene (0.31 mmol) in solvent (4 mL) for 24 h. [b]1 eq. , [c]1.25 eq. and [d]1.5 eq. of nitrosobenzene was used.

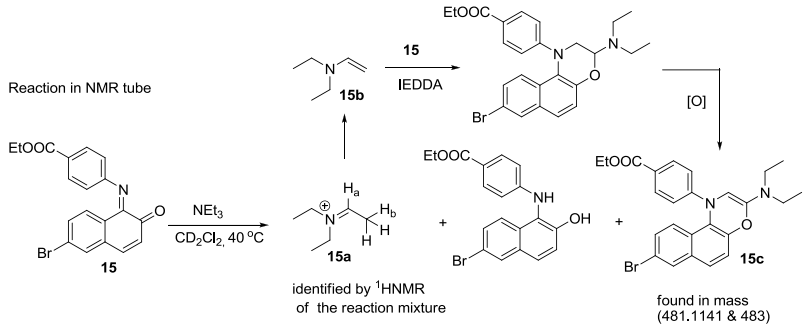
Figure s1: 1. ^{13}C NMR of isolated imminoquinone **15**. 2. ^{13}C NMR of the reaction mixture of 6-bromo-2-naphthol and ethyl 4-nitrosobenzoate in presence of NEt_3 in CD_2Cl_2 after 10 min.

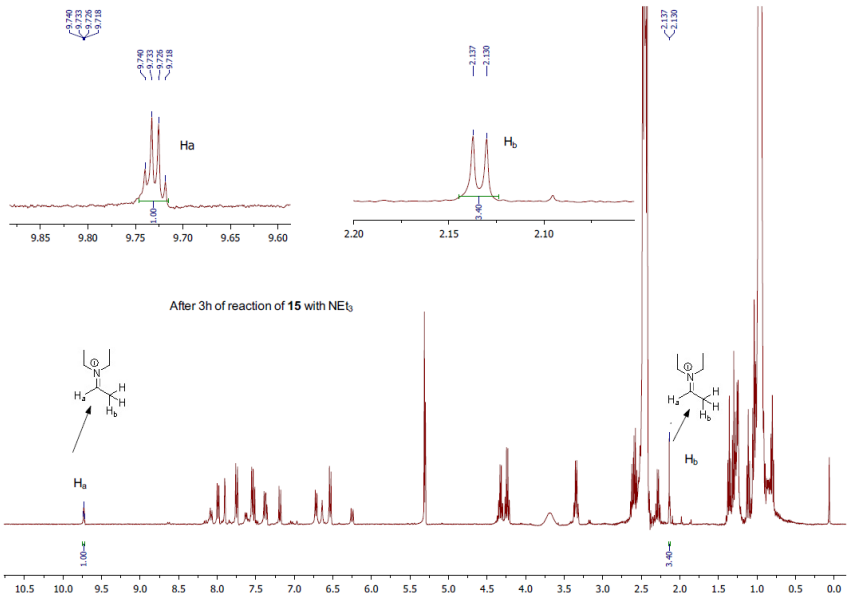


Scheme s1: Reaction with 1-naphthol.

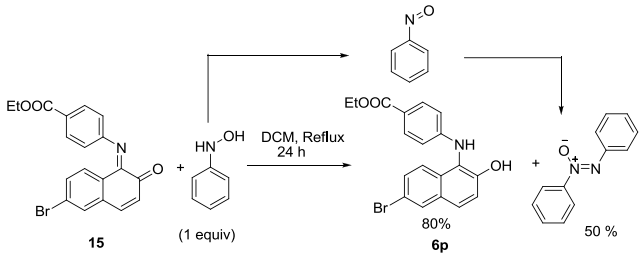


Scheme s2: Controlled experiments and detailed plausible mechanism.

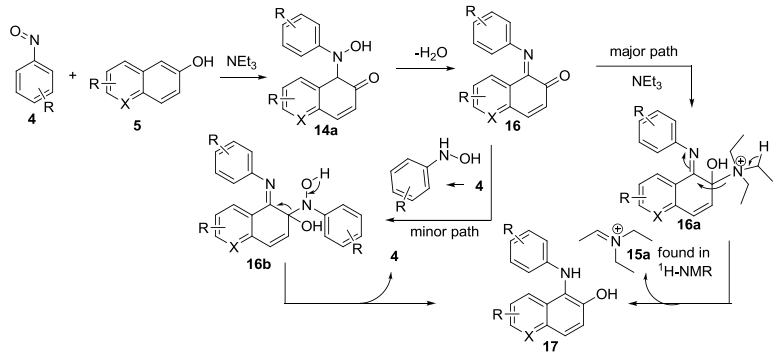




Reaction with phenyl hydroxyl amine:



Detailed mechanism:



Scheme s3: Possible mechanism for the formation of **22.**

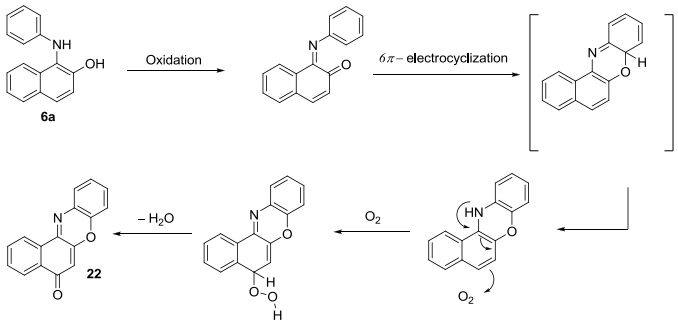


Figure s2: ThT assay based screening of molecules for their potency to inhibit the fibrillation kinetics of Aβ-40

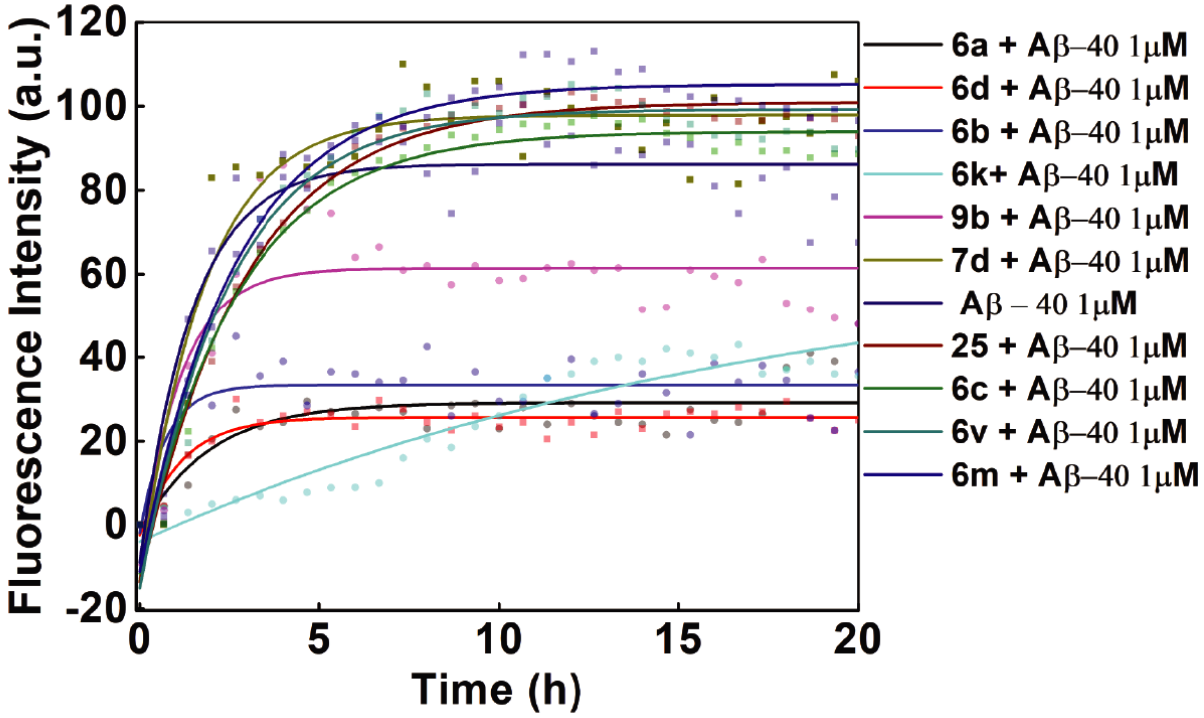
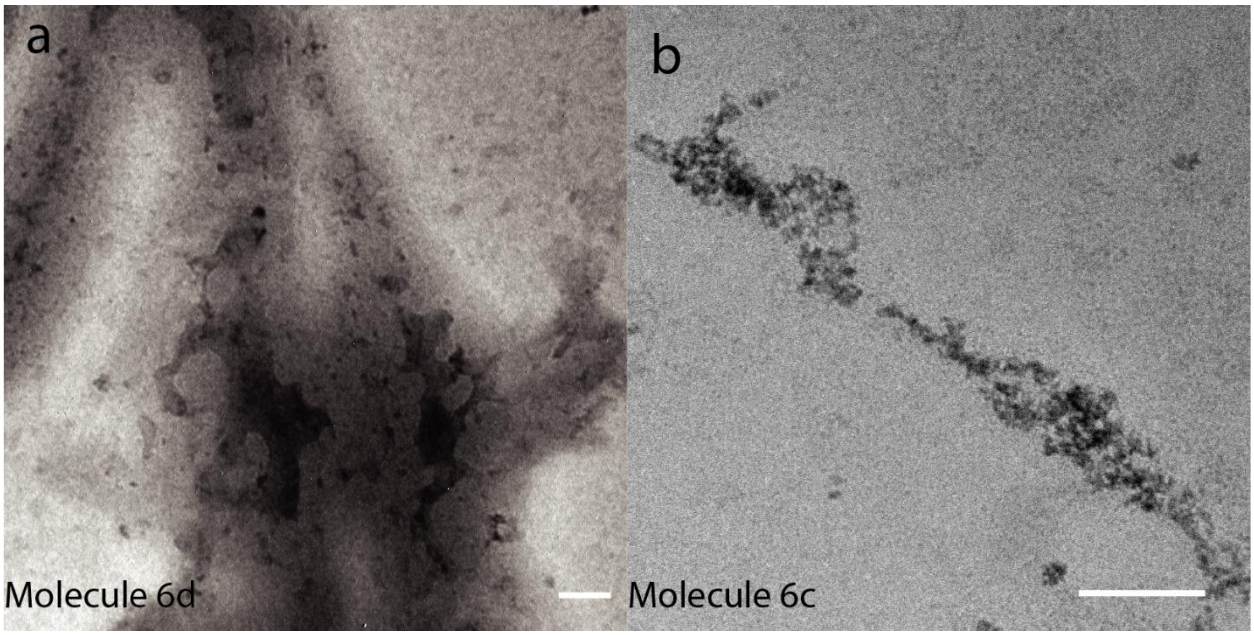


Figure s3: a & b. TEM micrograph of molecule 6d & 6c, respectively, incubated with Aβ-40 monomers for 24 hours. (Scale bars, 100nm)



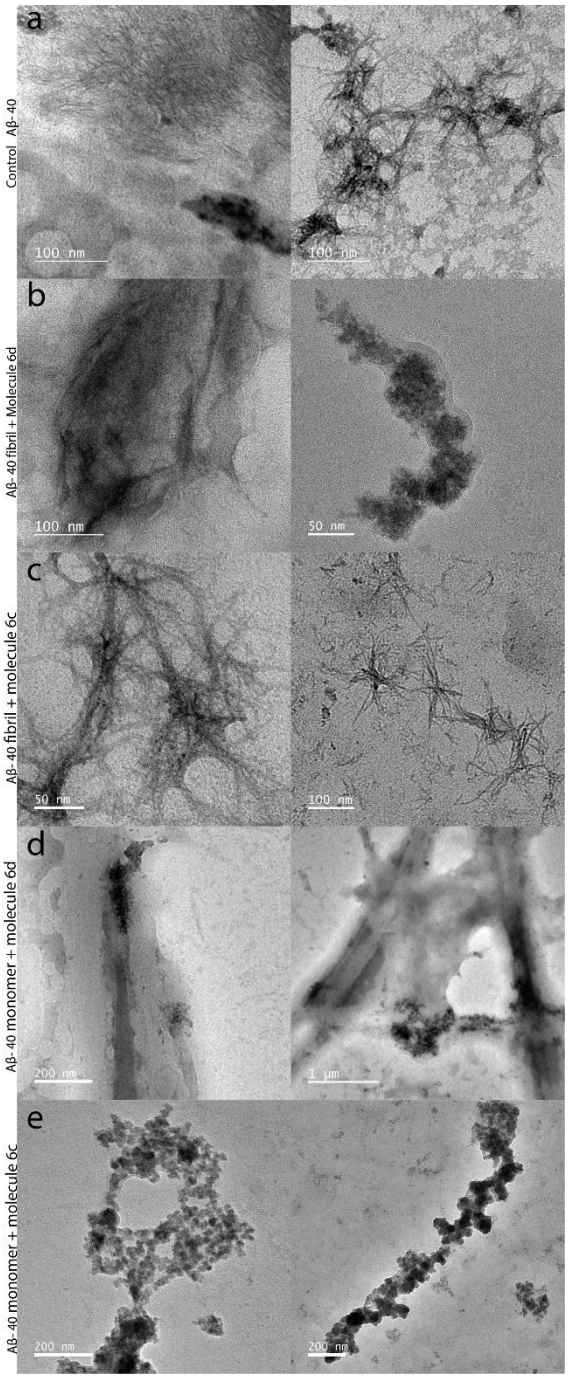
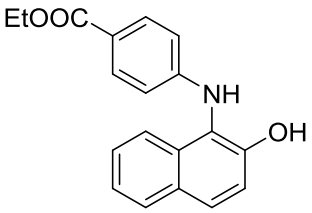


Figure s4: Changes in fibril morphology triggered by the molecule interaction observed by Transmission Electron Microscopy. **a.** Representative TEM micrographs for control Aβ-40 (untreated) **b.** Representative TEM micrographs of pre-formed Aβ-40 treated with molecule 6d and incubated for 24 hours showed no fibril like structures. **c.** Representative TEM micrographs of pre-formed Aβ-40 treated with molecule 6c and incubated for 24 hours showed fibril like structures albeit the networking between them was visibly less in comparison to the control **d.** Representative TEM micrographs of monomeric Aβ-40 treated with molecule **6d** and incubated for 24 hours were devoid of fibril like structures **e.** Representative TEM micrographs of monomeric Aβ-40 treated with molecule **6c** and incubated for 24 hours were devoid of fibril like structures.

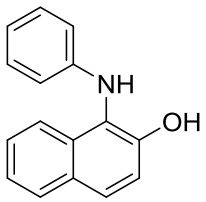
General procedure for the synthesis of aminated derivatives (GP-1):

Nitrosoarene (1.85 equiv) was added to a solution of naphthol/cyclohexadione/4-hydroxycumarine derivatives (0.14 – 0.34 mmol) and triethylamine (2 – 4 equiv) in dry dichloromethane or dry toluene (3 – 5 mL) and the reaction mixture was refluxed for 12 – 36 h under argon atmosphere. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under vacuum to obtain brown gummy residue which was further purified by column chromatography to afford analytically pure products.

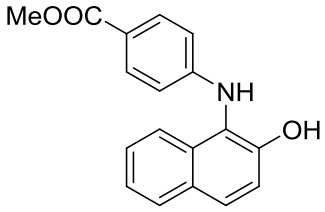
Ethyl 4-(2-hydroxynaphthalen-1-ylamino)benzoate (3): According to GP-1: 2-naphthol (25 mg, 0.17 mmol), ethyl 4-nitrosobenzoate (57 mg, 0.31 mmol) and NEt_3 (48 µL, 0.34 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **3** as a brown solid (45 mg, 85%). FTIR (KBr): $\tilde{\nu}$ = 3299, 2983, 1670, 1603, 1516, 1391, 1286, 1172, 769, 754 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.36 – 7.33 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 5.59 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.7, 152.0, 151.0, 132.0, 131.9, 129.82, 129.77, 128.9, 127.4, 123.9, 121.7, 121.5, 117.5, 117.3, 113.5, 60.7, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{18}NO_3^+$ ($[M + H]^+$): 308.1281; Found: 308.1278.



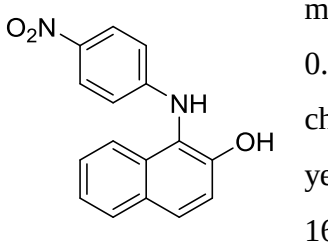
1-(phenylamino)naphthalen-2-ol (6a): According to GP-1: 2-naphthol (30 mg, 0.21 mmol), nitrosobenzene (41 mg, 0.32 mmol) and NEt_3 (58 µL, 0.42 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:10) of the crude gave **6a** as a white solid (29 mg, 58%). FTIR (KBr): $\tilde{\nu}$ = 3426, 1626, 1601, 1496, 1388, 1208, 749 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.35 – 7.32 (m, 2H), 7.21 – 7.17 (m, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 2H), 6.54 (s, 1H), 5.23 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.3, 146.8, 132.2, 129.80, 129.77, 129.3, 128.8, 127.2, 123.6, 121.6, 119.9, 118.7, 117.0, 114.4 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{14}NO^+$ ($[M + H]^+$): 236.1070 ; Found: 236.1073.



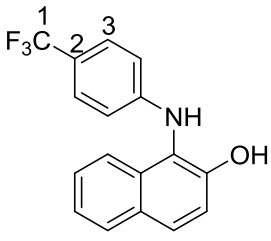
Methyl 4-(2-hydroxynaphthalen-1-ylamino)benzoate (6b): According to GP-1: 2-naphthol (25 mg, 0.17 mmol), methyl 4-nitrosobenzoate (57 mg, 0.31 mmol) and NEt_3 (48 µL, 0.34 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6b** as a brown solid (49 mg, 97%). FTIR (KBr): $\tilde{\nu}$ = 3385, 1695, 1606, 1518, 1282, 1172, 832, 768 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.82 (m, 3H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 6.63 – 6.60 (m, 2H), 6.42 (s, 1H), 5.64 (s, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.3, 151.9, 151.1, 132.0, 131.9, 131.8, 129.7, 128.8, 127.4, 123.9, 121.5, 117.5, 117.4, 114.0, 113.5, 52.0 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{16}NO_3^+$ ([M + H]$^+$): 294.1125; Found: 294.1127.



1-(4-nitrophenylamino)naphthalen-2-ol (6c): According to GP-1: 2-naphthol (35 mg, 0.24 mmol), 1-nitro-4-nitrosobenzene (68 mg, 0.45 mmol) and NEt_3 (68 µL, 0.49 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:3) of the crude gave **6c** as a yellow solid (54 mg, 80%). FTIR (KBr): $\tilde{\nu}$ = 3445, 2962, 2924, 2854, 1624, 1525, 1477, 1349, 1263, 1209, 812, 736 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 9.0 Hz, 2H), 7.86 – 7.87 (m, 2H), 7.59(d, *J* = 8.4 Hz, 1H), 7.45 – 7.43 (m, 1H), 7.39 – 7.37 (m, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 2H), 6.10 (s, 1H), 5.90 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.7, 151.7, 140.4, 131.7, 130.3, 129.8, 129.0, 127.8, 126.6, 124.2, 121.3, 117.6, 116.7, 113.4 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{13}N_2O_3$ ([M + H]$^+$): 281.0921; Found: 281.0921.

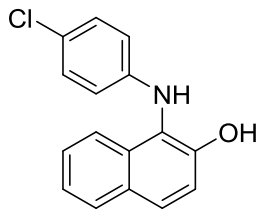


1-(4-(trifluoromethyl)phenylamino)naphthalen-2-ol (6d): According to GP-1: 2-naphthol (35 mg, 0.24 mmol), 1-(trifluoromethyl)-4-nitrosobenzene (79 mg, 0.45 mmol) and NEt_3 (68 µL, 0.49 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **6d** as yellow solid (61 mg, 83%). FTIR (KBr): $\tilde{\nu}$ = 3466, 3343, 2924, 1615, 1392, 1261, 1105, 816, 753 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.43 – 7.41

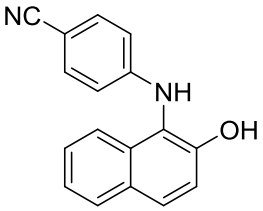


(m, 3H), 7.37 – 7.36 (m, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 2H), 6.30 (s, 1H), 5.49 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.1, 149.7, 131.9, 129.9, 129.8, 128.9, 127.5, 127.22 (C3), 127.20 (C3), 127.17 (C3), 127.15 (C3), 125.7 (C1), 123.95, 123.89 (C1), 122.1 (C2), 121.9 (C2), 121.7 (C2), 121.5 (C2), 121.4, 117.6, 117.3, 113.9 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{13}F_3NO^+$ ($[M + H]^+$): 304.0944; Found: 304.0949.

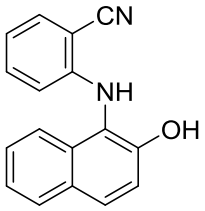
1-(4-chlorophenylamino)naphthalen-2-ol (6e): According to GP-1: 2-naphthol (25 mg, 0.17 mmol), 4-chlorobenzenamine (45 mg, 0.32 mmol), NEt_3 (48 µL, 0.35 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:10) of the crude gave **6e** as a brown gum (24 mg, 52%). FTIR (KBr): $\tilde{\nu}$ = 3438, 1632, 1262, 1092, 747 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81 (dd, *J* = 13.6, 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.42– 7.40 (m, 1H), 7.38 – 7.30 (m, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.44 (s, 1H), 5.26 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.2, 145.5, 132.0, 129.8, 129.7, 129.6, 128.9, 127.4, 124.7, 123.8, 121.4, 118.34, 117.1, 115.6 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{13}ClNO^+$ ($[M + H]^+$): 270.0680; Found: 270.0681.



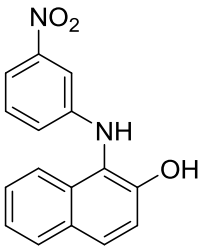
4-(2-hydroxynaphthalen-1-ylamino)benzonitrile (6f): According to GP-1: 2-naphthol (35 mg, 0.24 mmol), 4-aminobenzonitrile (59 mg, 0.45 mmol) and NEt_3 (68 µL, 0.49 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6f** as a brown solid (61 mg, 97%). FTIR (KBr): $\tilde{\nu}$ = 3378, 2220, 1606, 1511, 1471, 1388, 1318, 1135, 835, 822, 754 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 – 7.80 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.40 (m, 3H), 7.39 – 7.35 (m, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.4 Hz, 3H), 6.28 (s, 1H), 5.74 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.7, 150.5, 134.1, 131.6, 123.0, 129.6, 128.8, 127.5, 123.9, 121.1, 119.7, 117.2, 116.6, 114.1, 101.9 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{13}N_2O^+$ ($[M + H]^+$): 261.1022 ; Found: 261.1024.



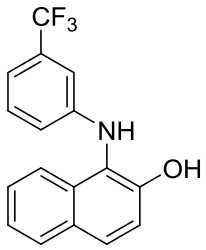
2-(2-hydroxynaphthalen-1-ylamino)benzonitrile (6g): According to GP-1: 2-naphthol (30 mg, 0.21 mmol), 2-aminobenzonitrile (51 mg, 0.38 mmol) and NEt_3 (58 µL, 0.42 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **6g** as a brown gum (28 mg, 52%). FTIR (KBr): $\tilde{\nu}$ = 3435, 2216, 1626, 1603, 1500, 1290, 1290, 1143, 816, 749 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.85 – 7.82 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.56 (dd, *J* = 7.8 Hz,1.2 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.38 – 7.35 (m, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.85 – 6.83 (m, 1H), 6.28 (d, *J* = 8.4 Hz, 1H), 6.26 (s, 1H), 6.07 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.0, 149.7, 134.8, 133.0, 131.7, 130.3, 129.8, 128.9, 127.7, 124.1, 121.2, 119.5, 117.7, 117.4, 116.5, 113.6, 97.4 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{13}N_2O^+$ ($[M + H]^+$): 261.1022; Found: 261.1031.



1-(3-nitrophenylamino)naphthalen-2-ol (6h): According to GP-1: 2-naphthol (35 mg, 0.24 mmol), 1-nitro-3-nitrosobenzene (68 mg, 0.45 mmol) and NEt_3 (68 µL, 0.49 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:4) of the crude gave **6h** as a yellow gum (48 mg, 70%). FTIR (KBr): $\tilde{\nu}$ = 3448, 1620, 1525, 1349, 1208, 814, 735, cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.86 – 7.83(m, 2H), 7.67 – 7.65 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 1.8 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.37 – 7.35 (m, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 7.29 (t, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 9.6 Hz, 1H), 6.34 (s, 1H), 5.59 (s, 1H).ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.1, 149.7, 148.1, 131.5, 130.5, 130.2, 129.9, 129.1, 127.6, 124.0, 121.2, 120.0, 117.35, 117.26, 114.7, 108.9 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{13}N_2O^+$ ($[M + H]^+$): 281.0921; Found: 281.0920.

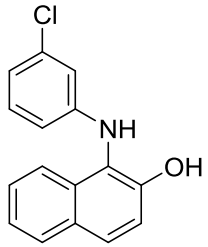


1-(3-(trifluoromethyl)phenylamino)naphthalen-2-ol (6i): According to GP-1: 2-naphthol (25 mg, 0.17 mmol), 3-(trifluoromethyl)benzenamine (56 mg, 0.32 mmol) and NEt_3 (48 µL, 0.31 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:6) of the crude gave **6i** as a white solid (41 mg, 78%). FTIR (KBr): $\tilde{\nu}$ = 3493, 1614, 1522, 1470, 1330, 1105, 816, 754 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.85 – 7.81 (m, 2H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.37 – 7.33 (m, 2H), 7.27 – 7.23 (m, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 6.70 (s, 1H), 6.35 (s, 1H), 5.43 (s, 1H) ppm. ^{13}C NMR (151 MHz,



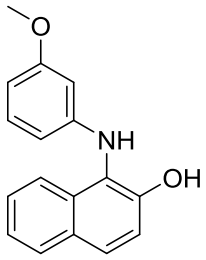
$CDCl_3$) δ = 152.2, 147.3, 132.2, 132.0, 131.9, 130.4, 129.8, 129.0, 127.5, 123.9, 121.3, 117.7, 117.21, 117.17, 116.6, 116.6, 116.5, 116.5, 111.09, 111.06, 111.04, 111.01 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{13}F_3NO^+$ ($[M + H]^+$): 304.0944; Found: 304.0950.

1-(3-chlorophenylamino)naphthalen-2-ol (6j): According to GP-1: 2-naphthol (25 mg, 0.17 mmol), 3-chlorobenzenamine (45 mg, 0.32 mmol) and NEt_3 (48 µL, 0.35 mmol) were reacted for

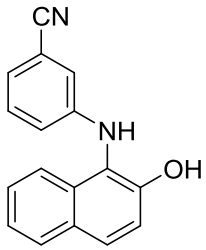


24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:15) of the crude gave **6j** as a brown gum (36 mg, 76%). FTIR (KBr): $\tilde{\nu}$ = 3372, 2963, 1625, 1598, 1479, 1396, 1264, 1143, 1095, 816, 748, 681 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.36 – 7.34 (m, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.81 – 6.80 (m, 1H), 6.62 – 6.61 (m, 1H), 6.53 – 6.51 (m, 1H), 6.42 (s, 1H), 5.28 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.2, 148.2, 135.6, 132.0, 130.8, 129.8, 129.7, 128.9, 127.4, 123.8, 121.4, 120.0, 117.9, 117.1, 114.3, 112.6 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{13}ClNO^+$ ($[M + H]^+$): 270.0680; Found: 270.0679.

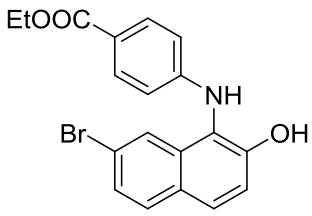
1-(3-methoxyphenylamino)naphthalen-2-ol (6k): According to GP-1: 2-naphthol (30 mg, 0.21 mmol), 3-methoxybenzenamine (53 mg, 0.38 mmol) and NEt_3 (58 µL, 0.42 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:10) of the crude gave **6k** as a brown gum (34 mg, 62%). FTIR (KBr): $\tilde{\nu}$ = 3442, 1619, 1601, 1487, 1392, 1206, 818 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.34 – 7.29 (m, 2H), 7.11 – 7.07 (m, 1H), 6.52 (s, 1H), 6.41 – 6.38 (m, 1H), 6.28 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.19 – 6.18(m, 1H), 5.26 (s, 1H), 3.70 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.2, 152.2, 148.3, 132.2, 130.6, 129.7, 129.3, 128.8, 127.2, 123.6, 121.6, 118.6, 117.1, 107.3, 104.9, 100.7, 55.3 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{16}NO_2^+$ ($[M + H]^+$): 266.1176; Found: 266.1185.



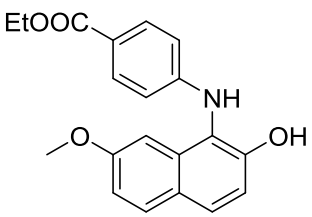
3-((2-hydroxynaphthalen-1-yl)amino)benzonitrile (6l): According to GP-1: 2-naphthol (35 mg, 0.24 mmol), 3-aminobenzonitrile (59 mg, 0.45 mmol) and NEt_3 (68 µL, 0.49 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:6) of the crude gave **6l** as a brown gum (36 mg, 58%). FTIR (KBr): $\tilde{\nu}$ = 3438, 2924, 2854, 2229, 1633, 1603, 1463, 1263, 680 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.84 (dd, *J* = 12.6, 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.43 –7.41 (m, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.84 (s, 1H), 5.49 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.9, 147.3, 131.6, 130.4, 129.9, 129.7, 128.9, 127.4, 123.8, 123.3, 121.0, 118.9, 118.6, 117.1, 117.0, 116.9, 113.4 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{13}N_2O^+$ ($[M + H]^+$): 261.1022 ; Found: 261.1030.



Ethyl 4-(2-bromo-7-hydroxynaphthalen-8-ylamino)benzoate (6m): According to GP-1: 7-bromo-2-naphthol (30 mg, 0.14 mmol), ethyl 4-nitrosobenzoate (57 mg, 0.25 mmol) and NEt_3 (38 µL, 0.27 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6m** as an off white solid (39 mg, 73%). FTIR (KBr): $\tilde{\nu}$ = 3421, 2924, 1662, 1604, 1442, 1262, 1107, 768 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 9.0 Hz, 2H), 7.78 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 5.61 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.8, 152.8, 150.4, 133.5, 132.0, 130.5, 129.7, 128.2, 127.4, 123.8, 122.2, 121.9, 117.9, 116.9, 113.4, 60.8, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{17}BrNO_3^+$ ($[M + H]^+$): 386.0386; Found: 386.0386.

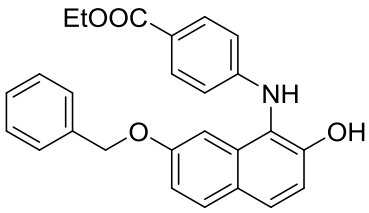


Ethyl 4-(2-hydroxy-7-methoxynaphthalen-1-ylamino)benzoate (6n): According to GP-1: 7-methoxy-2-naphthol (30 mg, 0.17 mmol), ethyl 4-nitrosobenzoate (57 mg, 0.31 mmol) and NEt_3 (48 µL, 0.34 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6n** as a white solid (47 mg, 80%). FTIR (KBr): $\tilde{\nu}$ = 3436, 2925, 1628, 1605, 1513, 1263, 1021, 830, 769 cm^{-1}. ^1H

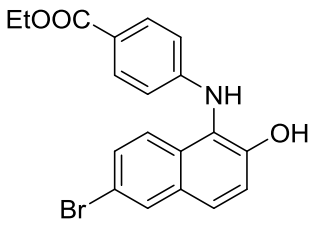


NMR (600 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 4.8 Hz, 1H), 7.70 (d, *J* = 4.8 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 11.4 Hz, 1H), 6.84 (s, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 5.58 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.8, 159.0, 152.6, 150.9, 133.4, 131.9, 130.5, 129.4, 125.0, 121.5, 116.9, 115.9, 114.6, 113.4, 100.7, 60.7, 55.3, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{20}H_{20}NO_4^+$ ([M + H]$^+$): 338.1387; Found: 338.1398.

Ethyl 4-(2-(benzyloxy)-7-hydroxynaphthalen-8-ylamino)benzoate (6o): According to GP-1: 7-(benzyloxy)-2-naphthol (40 mg, 0.16 mmol), ethyl 4-nitrosobenzoate (53 mg, 0.30 mmol) and NEt_3 (45 µL, 0.32 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6o** as a white solid (37 mg, 56%). FTIR (KBr): $\tilde{\nu}$ = 3354, 2979, 1689, 1607, 1517, 1283, 1263, 1105, 1018, 804, 767 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 9.0 Hz, 2H), 7.72 – 7.69 (m, 2H), 7.30 – 7.29 (m, 4H), 7.28 – 7.26 (m, 1H), 7.14 (d, *J* = 9.0 Hz, 1H), 7.06 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.92 (s, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 1H), 4.95 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.8, 158.2, 152.6, 150.9, 136.8, 133.4, 131.9, 130.5, 129.5, 128.7, 128.2, 127.6, 125.1, 121.6, 116.9, 116.5, 114.7, 113.4, 102.2, 70.1, 60.7, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{26}H_{24}NO_4^+$ ([M + H]$^+$): 414.1700 ; Found: 414.1695.

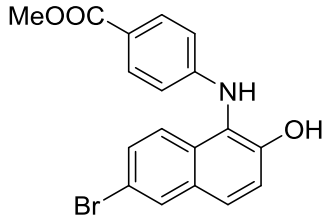


Ethyl 4-(2-bromo-6-hydroxynaphthalen-5-ylamino)benzoate (6p): According to GP-1: 6-bromo-2-naphthol (30 mg, 0.135 mmol), ethyl 4-nitrosobenzoate (45 mg, 0.25 mmol) and NEt_3 (38 µL, 0.27 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6p** as a brown solid (37 mg, 71%). FTIR (KBr): $\tilde{\nu}$ = 3345, 2985, 1685, 1633, 1600, 1515, 1281, 1173, 772 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.44 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 5.61 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.7, 152.3, 150.6, 131.9, 130.9, 130.8, 130.6, 128.8, 123.5, 121.9, 118.6, 117.8, 117.7, 113.5, 60.7, 14.6 ppm. Total count of ^{13}C is less than expected due to the merging of

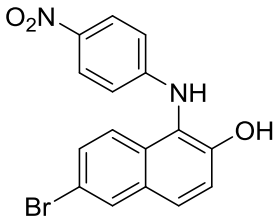


signal in the aromatic region. HRMS (ESI) exact mass calculated for $C_{19}H_{17}BrN_3O^+$ ([M + H]$^+$): 386.0386; Found: 386.0388.

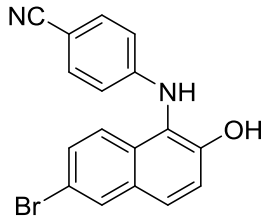
Methyl 4-(2-bromo-6-hydroxynaphthalen-5-ylamino)benzoate (6q): According to GP-1: 6-bromo-2-naphthol (35 mg, 0.16 mmol), methyl 4-nitrosobenzoate (48 mg, 0.29 mmol) and NEt_3 (44 µL, 0.31 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6q** as a brown solid (42 mg, 71%). FTIR (KBr): $\tilde{\nu}$ = 3334, 1712, 1693, 1605, 1518, 1434, 1282, 1173, 1108, 768 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 10.8 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 6.43 (s, 1H), 5.63 (s, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.2, 152.2, 150.7, 132.0, 130.9, 130.8, 130.6, 130.6, 128.8, 123.5, 121.5, 118.7, 117.8, 117.7, 113.5, 52.0 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{15}BrNO_3^+$ ([M + H]$^+$): 372.0230; Found: 372.0231.



1-(4-nitrophenylamino)-6-bromonaphthalen-2-ol (6r): According to GP-1: 6-bromo- 2-naphthol (40 mg, 0.18 mmol), 1-nitro-4-nitrosobenzene (51 mg, 0.34 mmol) and NEt_3 (50 µL, 0.36 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:3) of the crude gave **6r** as a light yellow solid (60 mg, 93%). FTIR (KBr): $\tilde{\nu}$ = 3370, 1594, 1499, 1466, 1264, 1111, 840 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 9.0 Hz, 2H), 8.00 (s, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.62 (d, *J* = 9.0 Hz, 2H), 5.92 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.3, 152.0, 140.6, 131.0, 130.9, 130.4, 129.4, 126.6, 123.2, 118.9, 118.0, 117.0, 113.6, 113.4 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{12}BrN_2O_3^+$ ([M + H]$^+$): 359.0026; Found: 359.0027.

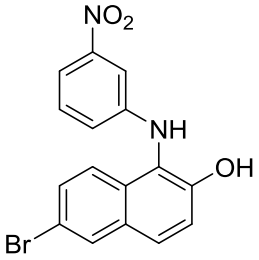


4-(2-bromo-6-hydroxynaphthalen-5-ylamino)benzonitrile (6s): According to GP-1: 6-bromo-2-naphthol (35 mg, 0.16 mmol), 4-aminobenzonitrile (38 mg, 0.29 mmol) and NEt_3 (44 µL, 0.31 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6s** as a brown solid (49 mg, 91%). FTIR (KBr): $\tilde{\nu}$ = 3436, 2213, 1607, 1515, 1361, 1172, 819 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.47 – 7.46 (m, 2H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.32 (d, *J* = 9.0 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.73



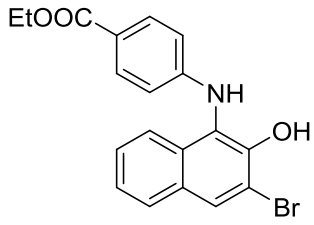
(s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.2, 150.4, 134.3, 130.9, 130.8, 130.4, 129.2, 123.3, 119.8, 118.7, 117.9, 117.1, 114.3, 102.3 ppm Total count of ^{13}C is less than expected due to the merging of signal in the aromatic region. HRMS (ESI) exact mass calculated for $C_{17}H_{12}BrN_2O^+$ ($[M + H]^+$): 339.0128; Found: 339.0124.

1-(3-nitrophenylamino)-6-bromonaphthalen-2-ol (6t): According to GP-1: 6-bromo-2-naphthol



(35 mg, 0.16 mmol), 1-nitro-3-nitrosobenzene (44 mg, 0.29 mmol) and NEt_3 (44 µL, 0.32 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc: Hexane, 1:4) of the crude gave **6t** as a yellow solid (41 mg, 73%). FTIR (KBr): $\tilde{\nu}$ = 3437, 1620, 1600, 1472, 1349, 735 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.67 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.47 – 7.46 (m, 3H), 7.34 (d, *J* = 9.0 Hz, 1H), 7.31 – 7.29 (m, 1H), 6.85 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.38 (s, 1H), 5.58 (s, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 152.4, 149.7, 147.8, 131.0, 130.9, 130.6, 130.4, 129.2, 123.2, 119.9, 118.7, 117.8, 117.6, 114.9, 108.9 ppm. Total count of ^{13}C is less than expected due to the merging of signal in the aromatic region. HRMS (ESI) exact mass calculated for $C_{16}H_{12}BrN_2O_3^+$ ($[M + H]^+$): 359.0026; Found: 359.0026.

Ethyl 4-(2-bromo-3-hydroxynaphthalen-4-ylamino)benzoate (6u): According to GP-1: 3-



bromo-2-naphthol (40 mg, 0.18 mmol), ethyl 4-nitrosobenzoate (60 mg, 0.34mmol) and NEt_3 (50 µL, 0.36 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6u** as a brown solid (53 mg, 76%). FTIR (KBr): $\tilde{\nu}$ = 3446, 1629, 1604, 1310, 1276, 1172, 748 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.43 – 7.35 (m, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 6.40 (s, 1H), 5.81 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.7, 150.5, 147.9, 131.8, 131.2, 131.1, 129.8, 127.9, 127.6, 125.0, 122.4, 122.1, 119.8, 113.9, 111.4, 60.7, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{17}BrN_3O^+$ ($[M + H]^+$): 386.0386; Found: 386.0392.

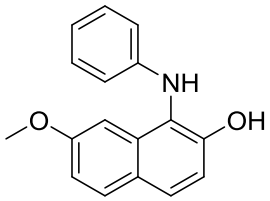
Methyl 4-(2-bromo-3-hydroxynaphthalen-4-ylamino)benzoate (6v): According to GP-1: 3-bromo-2-naphthol (35 mg, 0.16 mmol), methyl 4-nitrosobenzoate (48 mg, 0.29 mmol) and NEt_3 (44 µL, 0.31 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc: Hexane, 1:4) of the crude gave **6v** as a yellow solid (41 mg, 70%). FTIR (KBr): $\tilde{\nu}$ = 3355, 1681, 1603, 1582, 1457, 1432, 1175, 1134, 768, 755 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ = 8.37 (s, 1H), 8.21 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.35 – 7.32 (m, 1H), 6.51 – 6.45 (m, 2H), 3.73 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ = 166.4, 152.0, 148.9, 131.2, 131.0, 130.5, 128.9, 127.5, 127.0, 124.2, 122.3, 120.1, 117.8, 113.1, 112.7, 51.5 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{15}BrNO_3^+$ ($[M + H]^+$): 372.0230; Found: 372.0230.

Ethyl 4-(2-hydroxy-3-methoxynaphthalen-1-ylamino)benzoate (6w): According to GP-1: 3-methoxy-2-naphthol (35 mg, 0.20 mmol), ethyl 4-nitrosobenzoate (66 mg, 0.37 mmol) and NEt_3 (56 µL, 0.40 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6w** as a brown solid (55 mg, 82%). FTIR (KBr): $\tilde{\nu}$ = 3377, 2978, 1697, 1605, 1518, 1478, 1277, 1173, 1107, 770 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.13 (s, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.25 (s, 1H), 5.90 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.03 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.9, 150.9, 147.7, 142.1, 131.5, 128.8, 127.3, 127.0, 124.8, 124.6, 122.4, 120.8, 119.3, 113.7, 105.1, 60.5, 56.2, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{20}H_{20}NO_4^+$ ($[M + H]^+$): 338.1387; Found: 338.1389.

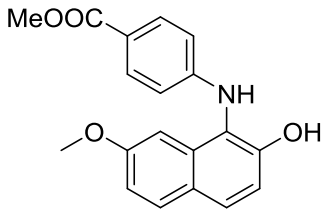
Methyl 4-(2-hydroxy-3-methoxynaphthalen-1-ylamino)benzoate (6x): According to GP-1: 3-methoxy-2-naphthol (35 mg, 0.20 mmol), methyl 4-nitrosobenzoate (61 mg, 0.37 mmol) and NEt_3 (56 µL, 0.40 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:4) of the crude gave **6x** as a orange yellow solid (61 mg, 95%). FTIR (KBr): $\tilde{\nu}$ = 3360, 1683, 1604, 1517, 1287, 1174, 1115, 770 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.68

(d, *J* = 8.4 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.32 – 7.30 (m, 1H), 7.14 (s, 1H), 6.61 (d, *J* = 9.0 Hz, 2H), 6.21 (s, 1H), 5.89 (s, 1H), 4.05 (s, 3H), 3.83 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.4, 151.0, 147.7, 142.1, 131.6, 128.8, 127.3, 127.0, 124.9, 124.6, 122.4, 120.5, 119.2, 113.7, 105.1, 56.3, 51.8 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{18}NO_4^+$ ($[M + H]^+$): 324.1230; Found: 324.1229.

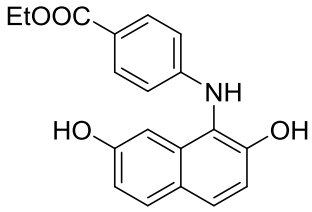
7-methoxy-1-(phenylamino)naphthalen-2-ol (6y): According to GP-1: 7-methoxy-2-naphthol (30 mg, 0.17 mmol), nitrosobenzene (34 mg, 0.32 mmol) and NEt_3 (48 µL, 0.34 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:10) of the crude gave **6y** as a white solid (26 mg, 56%). FTIR (KBr): $\tilde{\nu}$ = 3443, 1632, 1496, 1266, 1224, 749 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.72 – 7.69 (m, 2H), 7.19 – 7.15 (m, 3H), 6.97 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.92 (s, 1H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 2H), 6.57 (s, 1H), 5.16 (s, 1H), 3.71 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.9, 152.9, 146.7, 133.6, 130.4, 129.8, 129.0, 125.0, 119.9, 118.1, 115.7, 114.4, 114.3, 100.8, 55.3 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{16}NO_2^+$ ($[M + H]^+$): 266.1176 ; Found: 266.1178.



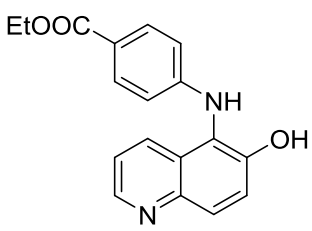
Methyl 4-(2-hydroxy-7-methoxynaphthalen-1-ylamino)benzoate (6z): According to GP-1: 7-methoxy-2-naphthol (35 mg, 0.20 mmol), methyl 4-nitrosobenzoate (61 mg, 0.37 mmol) and NEt_3 (56 µL, 0.40 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **6z** as a brown solid (57 mg, 88%). FTIR (KBr): $\tilde{\nu}$ = 3373, 1681, 1603, 1514, 1287, 1142, 808, 768 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 3.6 Hz, 1H), 7.70 (d, *J* = 3.6 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.84 (s, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 5.56 (s, 1H), 3.84 (s, 3H), 3.69 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.2, 159.1, 152.6, 150.9, 133.4, 131.9, 130.5, 129.5, 125.0, 121.3, 116.8, 116.0, 114.6, 113.5, 100.7, 55.4, 52.0 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{18}NO_4^+$ ($[M + H]^+$): 324.123; Found: 324.1222.



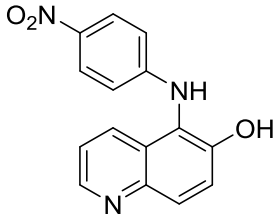
Ethyl 4-(2,7-dihydroxynaphthalen-8-ylamino)benzoate (6aa): According to GP-1: 7-hydroxy-2-naphthol (40 mg, 0.25 mmol), ethyl 4-nitrosobenzoate (83 mg, 0.46 mmol) and NEt_3 (69 µL, 0.50 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:2) of the crude gave **6aa** as a brown solid (54 mg, 67%). FTIR (KBr): $\tilde{\nu}$ = 3368, 2980, 1686, 1605, 1510, 1282, 1178, 1109, 830, 769 cm^{-1}. ^1H NMR (600 MHz, CD_3OD) δ = 7.75 (d, *J* = 9.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.86 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, CD_3OD) δ = 168.9, 157.3, 154.1, 153.2, 135.5, 132.2, 131.0, 129.0, 125.6, 119.3, 118.5, 116.3, 116.0, 113.7, 105.2, 61.3, 14.7 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{18}NO_4^+$ ($[M + H]^+$): 324.1230; Found: 324.1236.



Ethyl 4-(6-hydroxyquinolin-5-ylamino)benzoate (7a): According to GP-1: 6-hydroxy-quinoline (35 mg, 0.21 mmol), ethyl 4-nitrosobenzoate (68 mg, 0.38 mmol) and NEt_3 (59 µL, 0.41 mmol) were reacted for 36 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:1) of the crude gave **7a** as a brown solid (45 mg, 70%). FTIR (KBr): $\tilde{\nu}$ = 3403, 2965, 1904, 1689, 1606, 1479, 1369, 1204, 1134, 838, 807, 763 cm^{-1}. ^1H NMR (600 MHz, CD_3OD) δ = 8.64 (dd, *J* = 4.2, 1.2 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.40 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, CD_3OD) δ = 168.6, 153.5, 153.4, 148.0, 144.6, 133.0, 132.3, 129.1, 128.8, 123.6, 122.5, 120.1, 119.9, 113.8, 61.4, 14.7 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{17}N_2O_3^+$ ($[M + H]^+$): 309.1234; Found: 309.1236.

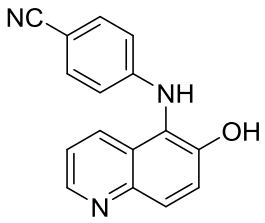


5-(4-nitrophenylamino)quinolin-6-ol (7b): According to GP-1: 6-hydroxyquinoline (30 mg, 0.21 mmol), 1-nitro-4-nitrosobenzene (58 mg, 0.38 mmol) and NEt_3 (57 µL, 0.41 mmol) were reacted for 36 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:1) of the crude gave **7b** as a brown solid (39 mg, 68%). FTIR (KBr): $\tilde{\nu}$ = 3366, 2962, 2206, 1605, 1513, 1469, 1261, 1081, 818, 805 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ = 10.31 (s, 1H), 9.00 (s, 1H), 8.72 (d, *J* = 5.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 2H), 7.92 (d, *J* = 9.6

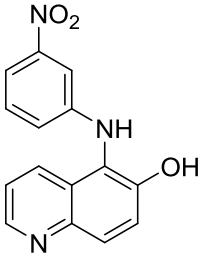


Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.44 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.63 – 6.45 (m, 2H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ = 153.8, 151.3, 147.5, 143.5, 137.0, 130.2, 129.1, 126.9, 126.1, 122.3, 121.8, 117.0, 112.4 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{12}N_3O_3^+$ ([M + H]$^+$): 282.0873; Found: 282.0884.

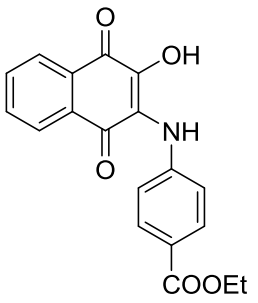
4-(6-hydroxyquinolin-5-ylamino)benzonitrile (7c): According to GP-1: 6-hydroxyquinoline (30 mg, 0.21 mmol), 4-aminobenzonitrile (50 mg, 0.38 mmol) and NEt_3 (57 µL, 0.41 mmol) were reacted for 36 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:1) of the crude gave **7c** as a brown solid (45 mg, 84%). FTIR (KBr): $\tilde{\nu}$ = 3366, 2962, 2206, 1605, 1513, 1469, 1261, 1081, 818, 805 cm^{-1}. ^{1}H NMR (600 MHz, CD_3OD) δ = 8.65 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 9.6 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.42 – 7.39 (m, 3H), 6.59 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (151 MHz, CD_3OD) δ = 153.4, 153.1, 148.1, 144.5, 134.6, 132.7, 129.10, 129.08, 123.6, 122.7, 121.2, 119.2, 114.7, 99.9 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{12}N_3O^+$ ([M + H]$^+$): 262.0975; Found: 262.0975.



5-(3-nitrophenylamino)quinolin-6-ol (7d): According to GP-1: 6-hydroxy-quinoline (50 mg, 0.34 mmol), 1-nitro-3-nitrosobenzene (96 mg, 0.63 mmol) and NEt_3 (95 µL, 0.68 mmol) were reacted for 36 h in dry DCM (5 mL). Column chromatography (silica; EtOAc : Hexane, 1:1) of the crude gave **7d** as a brown solid (65 mg, 68%). FTIR (KBr): $\tilde{\nu}$ = 3403, 2964, 1689, 1606, 1515, 1282, 1262, 1174, 807, 763 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 10.24 (s, 1H), 8.70 (d, *J* = 5.4 Hz, 1H), 8.33 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 9.6 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.24 (s, 1H), 6.90 (d, *J* = 7.8 Hz, 1H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ = 151.2, 148.84, 148.79, 147.6, 143.6, 130.6, 130.2, 128.5, 127.1, 122.4, 121.7, 119.8, 118.3, 111.5, 106.9 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{12}N_3O_3^+$ ([M + H]$^+$): 282.0873; Found: 282.0876.

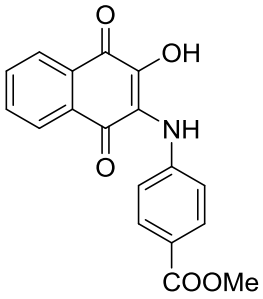


Ethyl 4-(1,4-dihydro-2-hydroxy-1,4-dioxonaphthalen-3-ylamino)benzoate (9a): According to



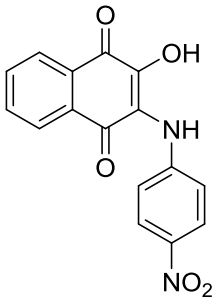
GP-1: 2-hydroxy-1,4-naphthoquinone (35 mg, 0.20 mmol), ethyl 4-nitrosobenzoate (67 mg, 0.37 mmol) and NEt_3 (56 µL, 0.40 mmol) were reacted for 36 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 2:1) of the crude gave **9a** as a light violet solid (46 mg, 67%). FTIR (KBr): $\tilde{\nu}$ = 3304, 2987, 1709, 1645, 1606, 1267, 1178, 1063, 765, 717 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ = 8.46 (s, 1H), 7.98 (t, *J* = 7.8 Hz, 2H), 7.80 – 7.78 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ = 181.8, 178.0, 165.7, 146.7, 145.0, 134.0, 133.7, 131.0, 130.5, 129.5, 125.8, 125.6, 124.0, 120.1, 117.3, 60.0, 14.4 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{16}NO_5^+$ ($[M + H]^+$): 338.1023; Found: 338.1026.

Methyl 4-(1,4-dihydro-2-hydroxy-1,4-dioxonaphthalen-3-ylamino)benzoate (9b): According



to GP-1: 2-hydroxy-1,4-naphthoquinone (35 mg, 0.20 mmol), methyl 4-nitrosobenzoate (61 mg, 0.37 mmol) and NEt_3 (56 µL, 0.40 mmol) were reacted for 36 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 2:1) of the crude gave **9b** as a light violet solid (36 mg, 55%). FTIR (KBr): $\tilde{\nu}$ = 3307, 2963, 1721, 1713, 1646, 1625, 1262, 1097, 1020, 800, 764 cm^{-1}. ^1H NMR (600 MHz, DMSO-d_6) δ = 8.43 (s, 1H), 7.99 – 7.96 (m, 2H), 7.80 – 7.78 (m, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.74 (s, 1H), 3.77 (s, 3H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ = 181.9, 180.0, 166.3, 146.8, 145.1, 134.0, 133.8, 131.1, 130.5, 129.6, 125.9, 125.6, 124.0, 119.8, 117.3, 51.6 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{12}NO_4^-$ ($[M – H]^-$): 322.0721; Found: 322.0726.

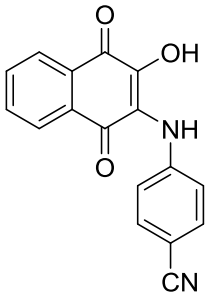
2-(4-nitrophenylamino)-3-hydroxynaphthalene-1,4-dione (9c): According to GP-1: 2-hydroxy-



1,4-naphthoquinone (35 mg, 0.20 mmol), 1-nitro-4-nitrosobenzene (57 mg, 0.37 mmol) and NEt_3 (56 µL, 0.40 mmol) were reacted for 36 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:1) of the crude gave **9c** as a light violet foam (37 mg, 59%). FTIR (KBr): $\tilde{\nu}$ = 3302, 2924, 1675, 1645, 1587, 1487, 1337, 1272, 1112, 1059, 719 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 8.88 (s, 1H), 8.04 (d, *J* = 9.2 Hz, 2H), 8.02 – 7.99 (m, 2H), 7.83 – 7.81(m, 2H), 6.87 (d, *J* = 9.2 Hz, 2H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ = 181.9, 180.8,

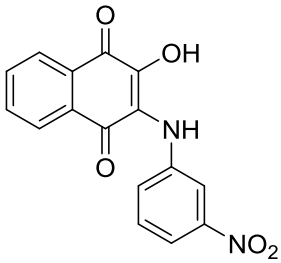
149.9, 148.0, 138.9, 134.7, 134.1, 131.6, 130.8, 126.3, 126.1, 125.1, 123.1, 116.8 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{11}N_2O_5^+$ ([M + H]$^+$): 311.0662; Found: 311.0663.

4-(1,4-dihydro-2-hydroxy-1,4-dioxonaphthalen-3-ylamino)benzonitrile (9d): According to



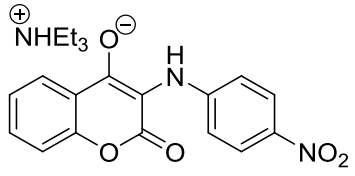
GP-1: 2-hydroxy-1,4-naphthoquinone (40 mg, 0.23 mmol), 4-aminobenzonitrile (56 mg, 42 mmol) and NEt_3 (64 µL, 0.46 mmol) were reacted for 36 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:1) of the crude gave **9d** as a violet solid (51 mg, 77%). FTIR (KBr): $\tilde{\nu}$ = 3301, 2220, 1645, 1604, 1579, 1326, 1267, 1237, 718 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.57 (s, 1H), 8.00 – 7.97 (m, 2H), 7.80 – 7.79 (m, 2H), 7.56 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ = 181.7, 180.2, 146.7, 146.2, 134.1, 133.7, 132.3, 131.2, 130.5, 125.8, 125.6, 123.3, 120.1, 117.7, 99.8 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_9N_2O_3^-$([M – H]$^-$): 289.0619; Found: 289.0629.

2-(3-nitrophenylamino)-3-hydroxynaphthalene-1,4-dione (9e): According to GP-1: 2-



hydroxy-1,4-naphthoquinone (35 mg, 0.20 mmol), 1-nitro-3-nitrosobenzene (57 mg, 0.37 mmol) and NEt_3 (56 µL, 0.40 mmol) were reacted for 36 h in dry DCM (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:1) of the crude gave **9e** as a purple solid (32 mg, 52%). FTIR (KBr): $\tilde{\nu}$ = 3300, 1649, 1625, 1533, 1350, 1331, 1263, 1232, 1097, 801, 718 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ = 8.50 (s, 1H), 8.00 – 7.97 (m, 2H), 7.80 – 7.79 (m, 2H), 7.64 – 7.63 (m, 2H), 7.44 – 7.41 (m, 1H), 7.24 (d, J = 9.0 Hz, 1H) ppm. ^{13}C NMR (151 MHz, DMSO-d_6) δ = 181.8, 180.0, 147.8, 144.1, 143.2, 133.9, 133.7, 131.0, 130.5, 128.9, 125.8, 125.6, 124.7, 124.2, 114.0, 112.4 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{11}N_2O_5^+$ ([M + H]$^+$): 311.0662; Found: 311.0660.

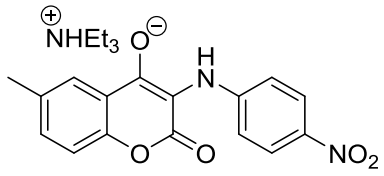
Triethylammonium 3-((4-nitrophenyl)amino)-2-oxo-2H-chromen-4-olate (11a): According to



GP-1: 4-hydroxycumarine (40 mg, 0.25 mmol), 1-nitro-4-nitrosobenzene (75 mg, 0.45 mmol) and NEt_3 (0.14 mL, 0.98 mmol) were reacted at 50 ^{o}C for 12 h in dry toluene (4 mL) and orange precipitate was obtained. The precipitate was filtered and washed with ethylacetate-hexane (1:2) to give **11a** as orange solid (65 mg, 66%). FTIR (KBr): $\tilde{\nu}$ = 3254, 1655, 1599, 1524, 1326, 1498, 1117, 1076, 759 cm^{-1}. ^{1}H NMR (600 MHz, CD_3OD) δ =

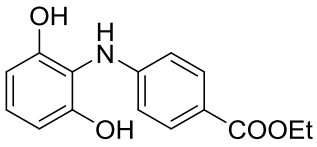
8.01 – 8.00 (m, 3H), 7.53 – 7.50 (m, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 3.19 (q, *J* = 7.2 Hz, 6H), 1.29 (t, *J* = 7.2 Hz, 9H) ppm. ^{13}C NMR (151 MHz, CD_3OD) δ = 173.3, 166.8, 155.9, 154.2, 138.2, 132.0, 126.8, 125.9, 124.3, 123.7, 117.2, 113.4, 102.9, 47.9, 9.2 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{11}N_2O_5^+$ ($[M + H]^+$): 299.0662; Found: 299.0667.

Triethylammonium 6-methyl-3-((4-nitrophenyl)amino)-2-oxo-2H-chromen-4-olate (11b):



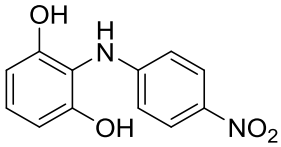
According to GP-1: 6-methyl-4-hydroxycumarine (40 mg, 0.23 mmol), 1-nitro-4-nitrosobenzene (64 mg, 0.42 mmol) and NEt_3 (0.13 mL, 0.98 mmol) were reacted at 50 °C for 12 h in dry toluene (4 mL) and orange precipitate was obtained. The precipitate was filtered and washed with ethyl acetate-hexane (1:2) to give **11b** as orange solid (60 mg, 63%). FTIR (KBr): $\tilde{\nu}$ = 3386, 1632, 1600, 1515, 1478, 1343, 1261, 1107, 804 cm^{-1}. ^{1}H NMR (600 MHz, CD_3OD) δ = 8.00 (d, *J* = 9.0 Hz, 2H), 7.80 (s, 1H), 7.34 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 9.0 Hz, 2H), 3.16 (q, *J* = 7.2 Hz, 6H), 2.41 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 9H) ppm. ^{13}C NMR (151 MHz, CD_3OD) δ = 173.4, 166.9, 155.9, 152.3, 138.1, 134.1, 133.0, 126.8, 125.6, 123.4, 117.1, 113.4, 102.9, 47.8, 21.0, 9.2 ppm. HRMS (APCI) exact mass calculated for $C_{16}H_{13}N_2O_5^+$ ($[M + H]^+$): 313.0819; Found: 313.0821.

Ethyl 4-(2,6-dihydroxyphenylamino)benzoate (13a): According to GP-1: cyclohexane-1,3-



dione (35 mg, 0.31 mmol), ethyl 4-nitrosobenzoate (0.10 g, 0.58 mmol) and NEt_3 (86 µL, 0.62 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (neutral alumina; EtOAc: Hexane, 1:1) of the crude gave **13a** as a colorless gum (39 mg, 46%). FTIR (KBr): $\tilde{\nu}$ = 3448, 1675, 1604, 1518, 1466, 1283, 1174, 1017, 770 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 9.0 Hz, 2H), 7.11 – 7.08 (m, 1H), 6.62 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.41 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.2, 154.2, 150.4, 131.8, 129.1, 121.7, 113.9, 113.6, 107.8, 60.9, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{16}NO_4^+$ ($[M + H]^+$): 274.1074; Found: 274.1075.

2-(4-nitrophenylamino)benzene-1,3-diol (13b): According to GP-1: cyclohexane-1,3- dione (30



mg, 0.27 mmol), 1-nitro-4-nitrosobenzene (75 mg, 0.49 mmol) and NEt_3 (74 µL, 0.53 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (neutral alumina; EtOAc : Hexane, 1:1) of the crude gave

13b as a light yellow gum (29 mg, 44%). FTIR (KBr): $\tilde{\nu}$ = 3403, 2924, 1596, 1498, 1480, 1306, 1260, 1113, 1013, 776 cm^{-1}. ^{1}H NMR (600 MHz, CD_3OD) δ = 8.02 (d, *J* = 9.0 Hz, 2H), 6.97 – 6.94 (m, 1H), 6.61 (d, *J* = 9.6 Hz, 2H), 6.43 (d, *J* = 8.4 Hz, 2H), 5.50 (s, 1H), 4.64 (s, 1H) ppm. ^{13}C NMR (151 MHz, CD_3OD) δ = 155.7, 155.3, 139.0, 128.5, 126.6, 115.5, 113.8, 108.1 ppm. HRMS (ESI) exact mass calculated for $C_{12}H_{11}N_2O_4^+$ ($[M + H]^+$): 247.0713; Found: 247.0718.

Ethyl 4-((3,5-dihydroxy-[1,1'-biphenyl]-4-yl)amino)benzoate (13c): According to GP-1: 5-phenyl-1,3-cyclohexanedione (35 mg, 0.18 mmol), ethyl 4-nitrosobenzoate (62 mg, 0.34 mmol) and NEt_3 (52 µL, 0.37 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (neutral alumina; EtOAc : Hexane, 1:2) of the crude gave **13c** as a colourless gum (30 mg, 46%). FTIR (KBr): $\tilde{\nu}$ = 3435, 2961, 2925, 1676, 1604, 1279, 1173, 1106, 1048, 800, 767 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.41 (m, 2H), 7.36 – 7.39 (m, 1H), 6.83 (s, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 5.44 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.1, 154.2, 150.3, 142.3, 140.4, 131.8, 129.0, 127.9, 127.1, 121.8, 113.6, 113.1, 106.7, 60.9, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{21}H_{20}NO_4^+$ ($[M + H]^+$): 350.1387; Found: 350.1391.

Ethyl 4-((3,5-dihydroxy-2-methyl-[1,1'-biphenyl]-4-yl)amino)benzoate (13d): According to GP-1: 4-Methyl-5-phenyl-1,3-cyclohexanedione[2] (35 mg, 0.17 mmol), ethyl 4-nitrosobenzoate (57 mg, 0.32 mmol) and NEt_3 (48 µL, 0.35 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (neutral alumina; EtOAc : Hexane, 1:1) of the crude gave **13d** as a colourless gum (26 mg, 38%). FTIR (KBr): $\tilde{\nu}$ = 3448, 2924, 2854, 1637, 1461, 1275, 1258, 750 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD) δ = 7.80 (d, *J* = 8.8 Hz, 2H), 7.42 –7.38 (t, *J* = 7.2 Hz, 2H), 7.33 – 7.29 (m, 3H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.35 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.04 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ppm. ^{13}C NMR (101 MHz, CD_3OD) δ = 168.9, 154.1, 153.7, 152.8, 143.5, 142.9, 132.0, 130.2, 129.0, 127.8, 120.1, 115.0, 114.6, 114.2, 109.4, 61.4, 14.7, 13.4 ppm**.** HRMS (ESI) exact mass calculated for $C_{22}H_{22}NO_4^+$ ($[M + H]^+$): 364.1543; Found: 364.1544.

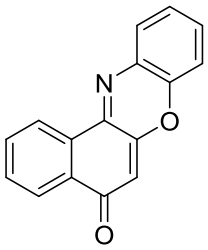
2-(3-nitrophenylamino)benzene-1,3-diol (13e): According to GP-1: cyclohexane-1,3- dione (30 mg, 0.27 mmol), 1-nitro-3-nitrosobenzene (75 mg, 0.49 mmol) and NEt_3 (74 µL, 0.53 mmol) were reacted for 24 h in dry DCM (4 mL). Column chromatography (neutral alumina; EtOAc : Hexane, 1:3) of the crude gave **13e** as a light yellow gum (32 mg, 49%). FTIR (KBr): $\tilde{\nu}$ = 3402, 2924, 1595, 1480, 1331, 1317, 1013, 839, 751 cm^{-1}. ^1H NMR (600 MHz, CD_3OD) δ = 7.29 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.18 – 7.17 (m, 1H), 7.08 – 7.06 (m, 1H), 6.78 – 6.77 (m, 1H), 6.75 – 6.72 (m, 1H), 6.24 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (151 MHz, CD_3OD) δ = 155.5, 150.5, 150.2, 130.2, 127.9, 121.2, 116.6, 112.9, 109.0, 108.1 ppm. HRMS (ESI) exact mass calculated for $C_{12}H_{11}N_2O_4^+$ ($[M + H]^+$): 247.0713; Found: 247.0719.

(4E)-ethyl 4-(6-bromo-2-oxonaphthalen-1(2H)-ylideneamino)benzoate (15): Ethyl 4-nitrosobenzoate (30 mg, 0.17 mmol) was added to a solution of 6-bromo-2-naphthol (20 mg, 0.09 mmol) and triethylamine (25 µL, 0.18 mmol) in dry dichloromethane (3 mL). The reaction mixture was stirred at room temperature under argon atmosphere. After 10 mins the solvent was immediately evaporated under vacuum at 30 °C to obtain green gum residue which was immediately purified by preparative TLC (ethyl acetate: hexane, 1:5) to afford **15** as green gum (18 mg, 52%). FTIR (KBr): $\tilde{\nu}$ = 2924, 1634, 1605, 1517, 1280, 1104, 767 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.66 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.56 (s, 1H), 7.40 (d, *J* = 9.6 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 6.31 (d, *J* = 10.2 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 179.2, 166.7, 156.9, 150.5, 143.5, 133.9, 133.6, 132.2, 132.1, 131.2, 129.9, 129.3, 127.3, 125.6, 115.5, 60.9, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{15}BrNO_3^+$ ($[M + H]^+$): 384.0230; Found: 384.0246.

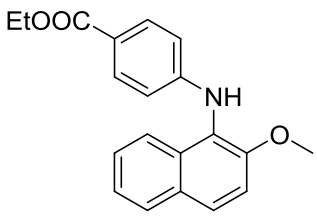
1-(diphenylamino)naphthalen-2-ol (21): Iodobenzene (38 µL, 0.34 mmol) was added to a solution of **6a** (40 mg, 017 mmol), Cs_2CO_3 (111 mg, 0.34 mmol) and CuI (6 mg, 0.034 mmol) in dry DMF (2 mL) under argon atmosphere. The mixture was stirred at 110 °C for 24 h. After completion of the reaction the solvent was removed under reduced pressure and the resulting mixture was extracted with dichloromethane (3×20 mL) and washed with $NaHCO_3$ (3×15 mL). The organic layers were dried

over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography (silica, EtOAc: hexane, 1:20) to give **21** as a brown solid (35 mg, 66%). FTIR (KBr): $\tilde{\nu}$ = 3449, 2961, 2921, 2851, 1632, 1492, 1467, 1261, 1023, 798, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.82 –7.79 (m, 2H), 7.72 – 7.70 (m, 1H), 7.35 – 7.28 (m, 3H), 7.23 – 7.19 (m, 4H), 7.12 – 7.10 (m, 4H), 6.96 – 6.93 (m, 2H), 5.88 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.0, 146.1, 132.7, 130.4, 129.8, 129.7, 128.7, 127.4, 124.0, 123.9, 122.8, 122.4, 120.4, 118.2 ppm. HRMS (ESI) exact mass calculated for $C_{22}H_{18}NO^+$ ($[M + H]^+$): 312.1400; Found: 312.1409.

12,12a-dihydrobenzo[a]phenoxazin-5-one (22): K_2CO_3 (47 mg, 0.34 mmol) was added to a solution of **6a** (40 mg, 0.17 mmol) in toluene (3 mL) and the mixture was stirred at 100 °C for 72 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica; EtOAc: Hexane, 1:10) gave **22** as light yellow solid (18 mg, 42%). FTIR (KBr): $\tilde{\nu}$ = 2959, 2923, 2853, 1736, 1637, 1596, 1457, 1306, 1261, 1102, 1024, 855, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.63 (d, *J* = 8.0 Hz, 1H), 8.21 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 9.2 Hz, 1H), 6.34 (s, 1H) ppm.^{13}C NMR (151 MHz, $CDCl_3$) δ = 184.2, 151.5, 147.6, 144.3, 133.0, 132.4, 132.3, 132.1, 131.8, 131.5, 130.1, 126.1, 125.5, 124.9, 116.1, 107.6 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{10}NO_2^+$ ($[M + H]^+$): 248.0700; Found: 248.0708.



Ethyl 4-(2-methoxynaphthalen-1-ylamino)benzoate (23a): Methyl iodide (24 µL, 0.39 mmol) was added to solution of **3** (40 mg, 0.13 mmol) and K_2CO_3 (90 mg, 0.65 mmol) in acetone (3 mL) and the mixture was stirred at 60 °C for 4 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica; EtOAc: Hexane, 1:5) gave **23a** as a brown solid (33 mg, 79%). FTIR (KBr): $\tilde{\nu}$ = 3322, 2979, 1687, 1600, 1580, 1365, 1287, 1169, 1097, 802, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) = 7.86 – 7.83 (m, 3H), 7.81 – 7.78 (m, 2H), 7.43 – 7.34 (m, 3H), 6.59 (d, *J* = 8.8 Hz, 2H), 6.10 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.9, 151.7, 151.2, 131.3, 131.0, 129.4, 128.4, 127.4, 126.8, 124.1, 123.3, 122.3, 120.5, 113.9, 113.5, 60.4, 56.6, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{20}H_{20}NO_3^+$ ($[M + H]^+$): 322.1438; Found: 322.1433.



6-methoxy-*N*-(3-nitrophenyl)quinolin-5-amine (23b): Methyl iodide (33 µL, 0.53 mmol) was added to solution of **7d** (50 mg, 0.18 mmol) and K_2CO_3 (0.12 g, 0.89 mmol) in acetone (4 mL) and the mixture was stirred at 60 °C for 4 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica; EtOAc: Hexane, 1:2) gave **23b** as a brown solid (30 mg, 57%). FTIR (KBr): $\tilde{\nu}$ = 3399, 3376, 2924, 2852, 1618, 1590, 1526, 1356, 1319, 1264, 1097, 1060, 807, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.83 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.12 – 8.09 (m, 2H), 7.64 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.43 – 7.42 (m, 1H), 7.33 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 6.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.07 (s, 1H), 3.97 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.7, 149.5, 148.9, 148.1, 144.2, 131.4, 130.0, 129.0, 126.1, 121.8, 121.7, 120.5, 116.6, 114.2, 109.4, 56.7 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{14}N_3O_3^+$ ($[M + H]^+$): 296.1030; Found: 296.1033.

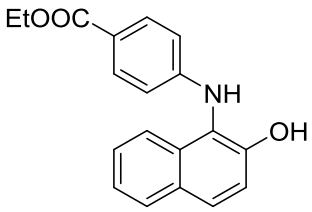
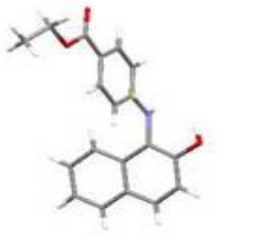
1-(4-(ethoxycarbonyl)phenylamino)naphthalen-2-yl trifluoromethanesulfonate (24): Trifluoromethanesulfonic anhydride (26 µL, 0.16 mmol) was added to a solution of **3** (40 mg, 0.13 mmol) in pyridine (0.5 mL) at 0 °C and the reaction mixture was stirred for 18 h at room temperature. Aq. NH_4OH solution (10 mL) and 2 N HCl (0.2 mL) were added to the reaction mixture and extracted with dichloromethane (3×15 mL). The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by column chromatography (silica, EtOAc: hexane, 1:5) to give **24** as a colorless solid (35 mg, 61%). FTIR (KBr): $\tilde{\nu}$ = 3307, 1688, 1606, 1583, 1510, 1466, 1423, 1290, 1259, 1142, 829, 753 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.96 – 7.94 (m, 2H), 7.89 – 7.87 (m, 3H), 7.61 – 7.58 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 1H), 6.61 (d, *J* = 9.0 Hz, 2H), 6.16 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.7, 149.4, 143.0, 133.7, 131.5, 131.3, 128.9, 128.8, 128.7, 128.0, 127.7, 124.4, 121.8, 120.0, 119.8, 117.7, 113.9, 60.7, 14.6 ppm. HRMS (ESI) exact mass calculated for $C_{20}H_{17}F_3NO_5S^+$ ($[M + H]^+$): 440.0774; Found: 440.0774.

Gram scale synthesis:

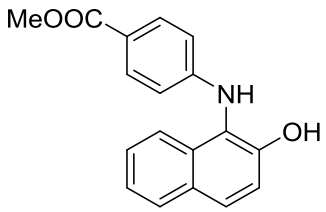
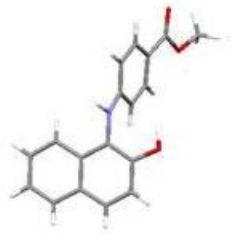
Ethyl 4-nitrosobenzoate (2.3 g, 12.85 mmol) was added to a solution of 2-naphthol (1 g, 6.95 mmol) and triethylamine (1.93 mL, 13.9 mmol) in dry dichloromethane (100 mL) and the reaction

mixture was refluxed for 24 h under argon atmosphere. The reaction mixture was allowed to cool to room temperature and dichloromethane was evaporated under vacuum to obtain brown solid residue which was further purified by column chromatography (silica, EtOAc: hexane, 1:5) to afford **3** as a brown solid (1.53 g, 71%).

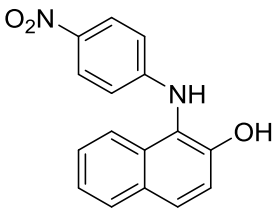
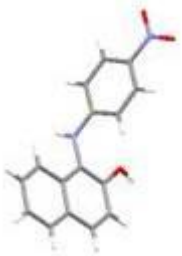
Crystal of **3** (CCDC 1866324):

	
Empirical formula	$C_{19}H_{17}NO_3$
Formula weight	61.47
Crystal habit, colour	Block, Brown
Crystal size, mm^3	0.38X 0.33X 0.31
Temperature, T	296(2)
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*P 21/c*
Unit cell dimensions	a = 11.7960(11)Å b = 11.9194(12)Å c = 11.1919(10) α = 90°, β = 90.881(6)°, γ = 90°,
Volume, V(Å^3)	1573.4(3)
Z	20
Calculated density, $Mg \cdot m^{-3}$	1.297
Absorption coefficient, μ(mm^{-1})	0.088
F(000)	648
θ range for data collection	1.727° to 25.046°
Limiting indices	$-14 \leq h \leq 13$, $-14 \leq k \leq 13$, $-13 \leq l \leq 13$
Reflection collected / unique	16900/ 1943 [R(int) = 0.0361]
Completeness to θ	97.6% (θ = 25.242°)
Refinement method	SHELXL-2013 (Sheldrick, 2013)
Data / restraints / parameters	1943/ 0 / 214
Goodness−of−fit on F^2	1.050
Final R indices [I>2sigma(I)]	$R1$ = 0.0500, $wR2$ = 0.1290
R indices (all data)	$R1$ = 0.0721, $wR2$ = 0.1432
Largest diff. peak and hole	0.287 and -0.221e·Å^{-3}

Crystal **6b** (CCDC 1866321):

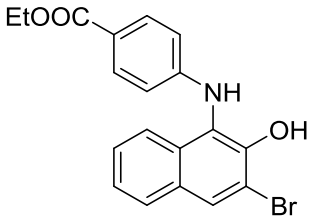
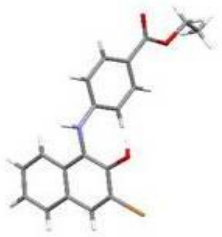
	
Empirical formula	C_{18} H_{15} N O_3
Formula weight	40.46
Crystal habit, colour	Needle, Brown
Crystal size, mm^3	0.31 X 0.26 X 0.21
Temperature, *T*	296(2)
Wavelength, λ(Å)	0.71073
Crystal system	orthorhombic
Space group	*P b c a*
Unit cell dimensions	*a* = 13.692(3) Å *b* = 9.810(2) Å *c* = 21.438(5) Å α = 90°, β = 90°, γ = 90°,
Volume, *V*($Å^3$)	2879.4(11)
Z	58
Calculated density, $Mg \cdot m^{-3}$	1.353
Absorption coefficient, μ(mm^{-1})	0.093
F(000)	1232
θ range for data collection	1.90 ° to 25.05 °
Limiting indices	$-14 \leq h \leq 16$, $-11 \leq k \leq 11$, $-25 \leq l \leq 20$
Reflection collected / unique	17752/ 1819 [*R*(int) = 0.0476]
Completeness to θ	97.4% (θ = 25.242°)
Refinement method	SHELXL-2013 (Sheldrick, 2013)
Data / restraints / parameters	1819 / 0 / 205
Goodness–of–fit on F^2	1.053
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0463, *wR*2 = 0.1193
R indices (all data)	*R*1 = 0.0661, *wR*2 = 0.1312
Largest diff. peak and hole	0.209 and -0.184e·$Å^{-3}$

Crystal of **6c** (CCDC 1866312):

	
Empirical formula	C_{16} H_{12} N_2 O_3
Formula weight	280.0848

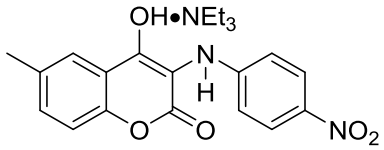
Crystal habit, colour	Needle, yellow
Crystal size, mm^3	0.35 X 0.28X 0.23
Temperature, *T*	293(2)
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*P 21/c*
Unit cell dimensions	*a* = 5.4752(8) Å *b* = 17.649(2)Å *c* = 13.8907(17) Å α = 90°, β = 94.311(15) °, γ = 90°,
Volume, *V*($Å^3$)	1338.5(3)
Z	4
Calculated density, $Mg \cdot m^{-3}$	1.391
Absorption coefficient, μ(mm^{-1})	0.098
F(000)	584
θ range for data collection	2.94 ° to 25.00°
Limiting indices	$-3 \le h \le 6$, $-20 \le k \le 18$, $-16 \le l \le 16$
Reflection collected / unique	4555 / 1208 [*R*(int) = 0.0412]
Completeness to θ	97.8% (θ = 25.00 °)
Refinement method	SHELXL-97 (Sheldrick, 1997)
Data / restraints / parameters	1208 / 0 / 196
Goodness–of–fit on F^2	0.963
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0775, *wR*2 = 0.1733
R indices (all data)	*R*1 = 0.1361, *wR*2 = 0.2356
Largest diff. peak and hole	0.242 and $-0.225 e \cdot Å^{-3}$

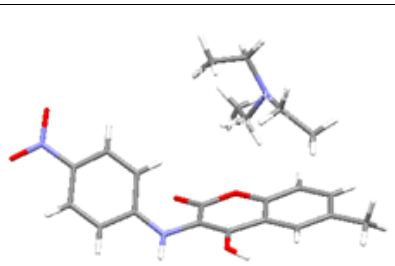
Crystal of **6u** (CCDC 1866323):

	
Empirical formula	$C_{19}H_{16}BrNO_3$
Formula weight	386.24
Crystal habit, colour	Block, Brown
Crystal size, mm^3	0.41 X 0.36 X 0.31
Temperature, *T*	293(2)
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*P 21/c*
Unit cell dimensions	*a* = 11.6484(7)Å *b* = 13.0417(5) Å *c* = 11.0000(6) Å α = 90°, β = 91.035(5) °, γ = 90°,
Volume, *V*($Å^3$)	1670.79(15)
Z	4

Calculated density, Mg·m^{-3}	1.535
Absorption coefficient, μ(mm^{-1})	2.477
F(000)	784
θ range for data collection	2.97 ° to 25.00°
Limiting indices	$-12 \le h \le 13$, $-15 \le k \le 15$, $-13 \le l \le 12$
Reflection collected / unique	6195/ 2030 [R(int) = 0.0423]
Completeness to θ	98.5% (θ = 25.00°)
Refinement method	'SHELXL–97 (Sheldrick, 1997)
Data / restraints / parameters	2030 / 0 / 223
Goodness–of–fit on F^2	1.060
Final R indices [I>2sigma(I)]	$R1$ = 0.0501, $wR2$ = 0.1238
R indices (all data)	$R1$ = 0.0819, $wR2$ = 0.1489
Largest diff. peak and hole	0.302 and –0.622·Å^{-3}

Crystal of **11b** (CCDC 1866300):

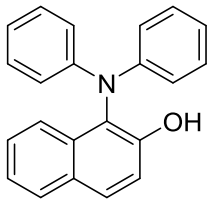




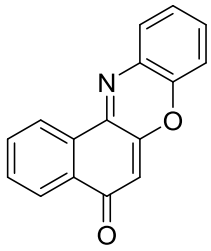
Empirical formula	C_{22} H_{27} N_3 O_5
Formula weight	413.47
Crystal habit, colour	Needle, Orange
Crystal size, mm^3	0.28 X 0.25 X 0.22
Temperature, T	293(2)
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*P 21/c*
Unit cell dimensions	a = 19.306(3)Å b = 10.033(2)Å c = 11.1506(14)Å α = 90°, β = 93.091(13)°, γ = 90°,
Volume, V(Å^3)	2156.7(6)
Z	4
Calculated density, Mg·m^{-3}	1.273
Absorption coefficient, μ(mm^{-1})	0.091
F(000)	880
θ range for data collection	2.89° to 25.00 °
Limiting indices	$-22 \le h \le 22$, $-11 \le k \le 11$, $-12 \le l \le 13$
Reflection collected / unique	15558 / 2079 [R(int) = 0.1142]
Completeness to θ	99.3% (θ = 25.00°)
Refinement method	SHELXL-97 (Sheldrick, 1997)
Data / restraints / parameters	2070/ 0 / 276
Goodness–of–fit on F^2	1.795
Final R indices [I>2sigma(I)]	$R1$ = 0.2241, $wR2$ = 0.5229
R indices (all data)	$R1$ = 0.2791, $wR2$ = 0.5529

Largest diff. peak and hole	1.048 and – 0.522 $Å^{-3}$

Crystal of **21** (CCDC 1866322):

	
Empirical formula	C_{22} H_{17} N O
Formula weight	311.37
Crystal habit, colour	Needle, brown
Crystal size, mm^3	0.34 X 0.28X 0.24
Temperature, *T*	293(2)
Wavelength, λ(Å)	0.71073
Crystal system	orthorhombic
Space group	*P 21 21 21*
Unit cell dimensions	*a* = 10.4148(15) Å *b* = 10.5315(9) Å *c* = 15.0526(18)Å α = 90°, β = 90 °, γ = 90°,
Volume, *V*($Å^3$)	1651.0(3)
Z	4
Calculated density, $Mg \cdot m^{-3}$	1.253
Absorption coefficient, μ(mm^{-1})	0.076
F(000)	656
θ range for data collection	3.33 ° to 24.99 °
Limiting indices	$-12 \leq 12 \leq 4, -12 \leq k \leq 11, -17 \leq l \leq 10$
Reflection collected / unique	4179 / 1282 [*R*(int) = 0.0432]
Completeness to θ	99.6% (θ = 24.99 °)
Refinement method	SHELXL-97 (Sheldrick, 1997
Data / restraints / parameters	4179 / 0 / 218
Goodness–of–fit on F^2	1.004
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0669, *wR*2 = 0.0983
R indices (all data)	*R*1 = 0.1505, *wR*2 = 0.1412
Largest diff. peak and hole	0.166 and –0.165$Å^{-3}$

Crystal of **22** (CCDC 1866319):

	
Empirical formula	C_{16} H_9 N O_2
Formula weight	247.24
Crystal habit, colour	Needle, yellow
Crystal size, mm^3	0.36 X 0.34X 0.32
Temperature, *T*	296(2)
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*P 21/n*
Unit cell dimensions	*a* = 3.9089(13) Å *b* = 23.323(8) Å *c* = 12.350(4) Å α = 90°, β = 94.388(4)°, γ = 90°,
Volume, *V*($Å^3$)	1122.6(6)
Z	4
Calculated density, $Mg \cdot m^{-3}$	1.463
Absorption coefficient, μ(mm^{-1})	0.098
F(000)	512
θ range for data collection	1.746° to 24.997°
Limiting indices	$-4 \le h \le 4$, $-27 \le k \le 27$, $-14 \le l \le 14$
Reflection collected / unique	25762/ 1531 [*R*(int) = 0.0584]
Completeness to θ	97.5% (θ = 25.242°)
Refinement method	SHELXL-2013 (Sheldrick, 2013)
Data / restraints / parameters	1531 / 0 / 172
Goodness–of–fit on F^2	1.051
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0416, *wR*2 = 0.0972
R indices (all data)	*R*1 = 0.0587, *wR*2 = 0.1112
Largest diff. peak and hole	0.146 and $-0.164 \cdot Å^{-3}$

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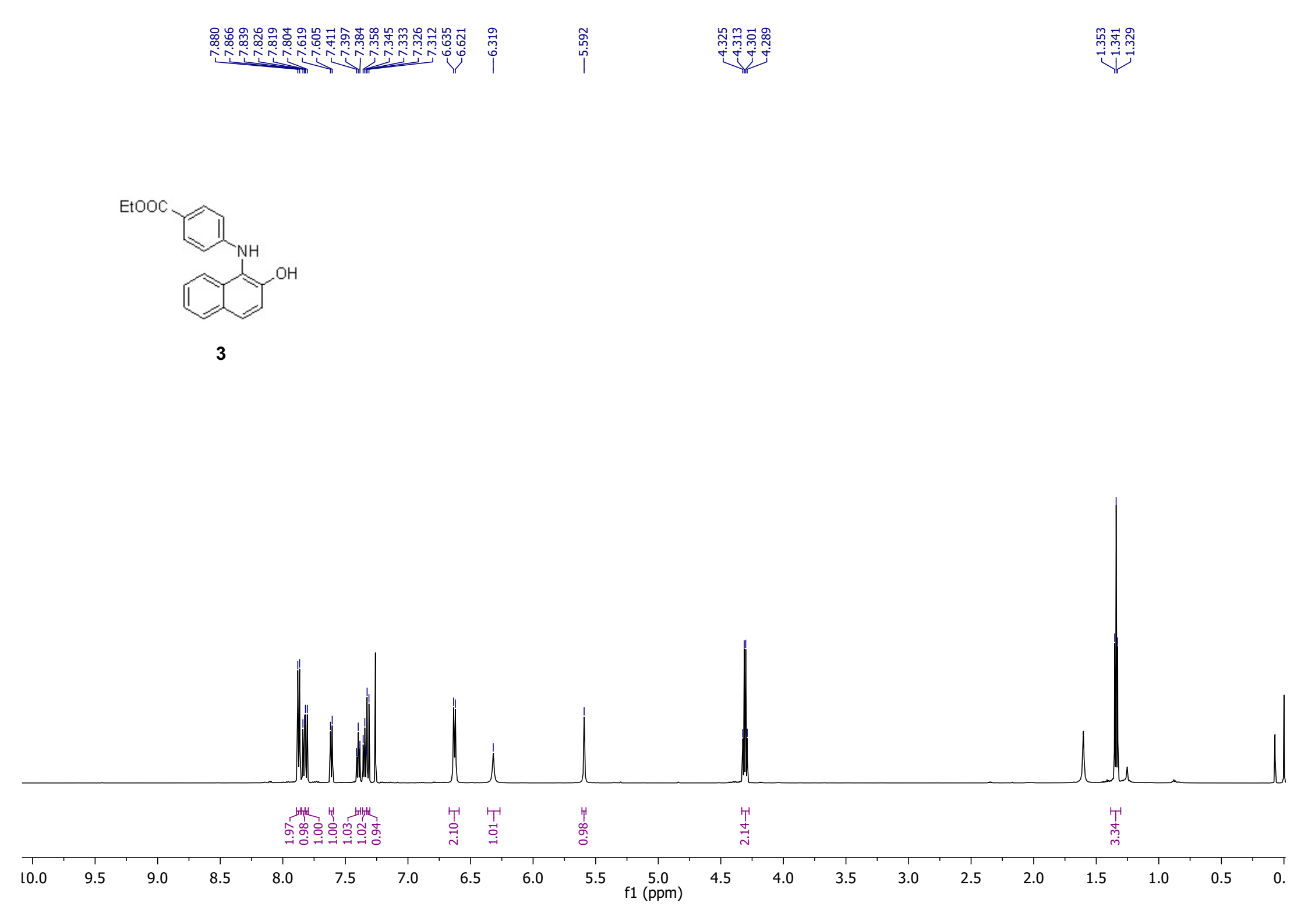
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7.826
7.819
7.804
7.619
7.605
7.411
7.397
7.384
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7.345
7.333
7.326
7.312
6.635
6.621
6.319
5.592
4.325
4.313
4.301
4.289
1.353
1.341
1.329
EtOOC
NH
OH
1.97
0.98
1.00
1.00
1.03
1.02
0.94
2.10
1.01
0.98
2.14
3.34
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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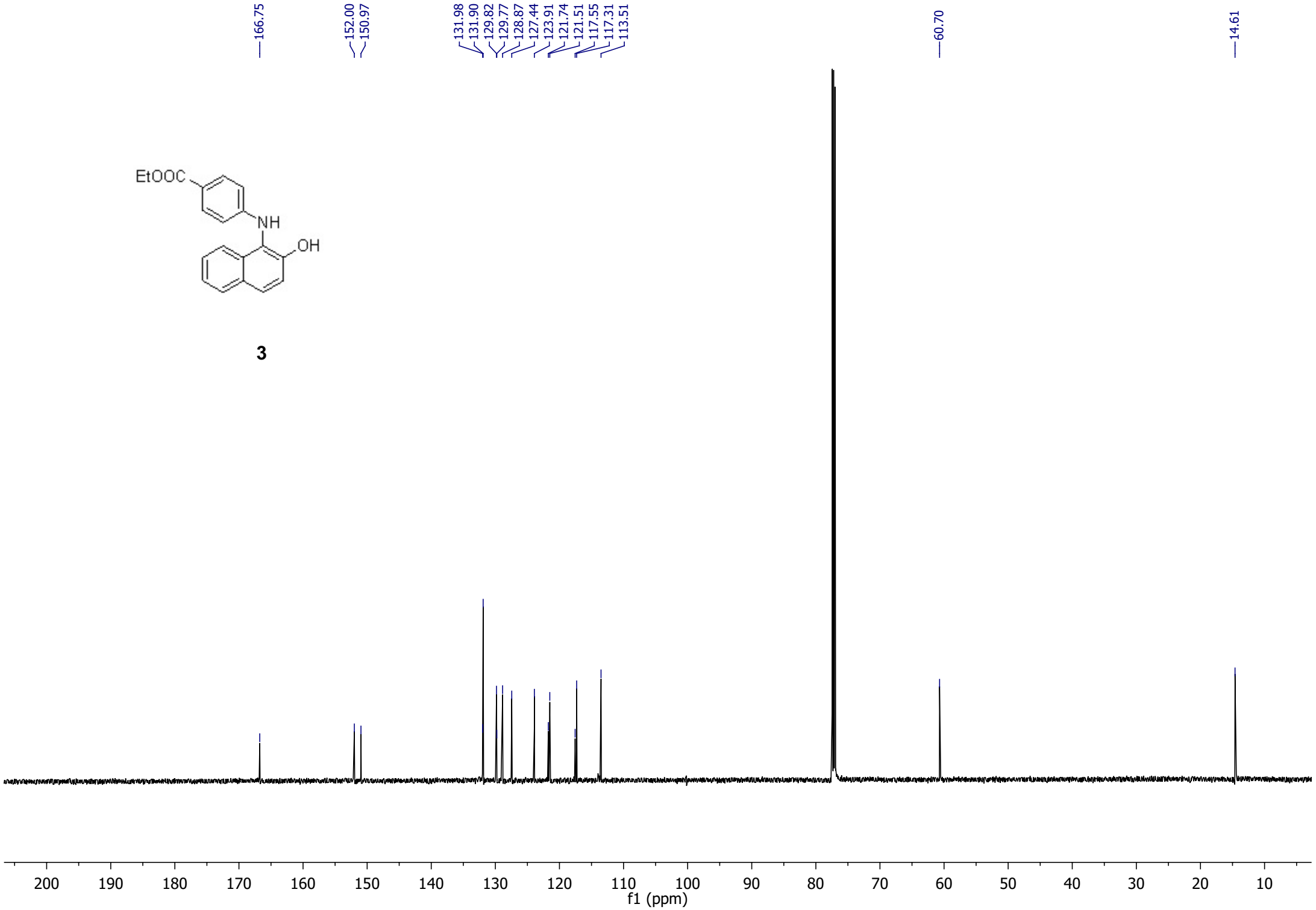
1.5
1.0
0.5
0.
f1 (ppm)

3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128.87
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123.91
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117.31
113.51
60.70
14.61
EtOOC
NH
OH
3
200
190
180
170
160
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140
130
120
110
100
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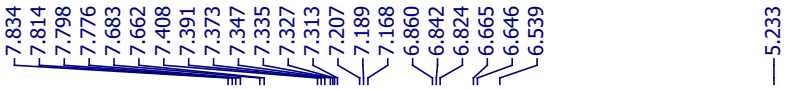
80
70
60
50
40
30
20
10
f1 (ppm)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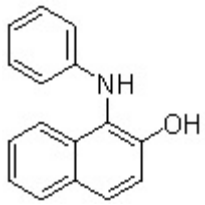
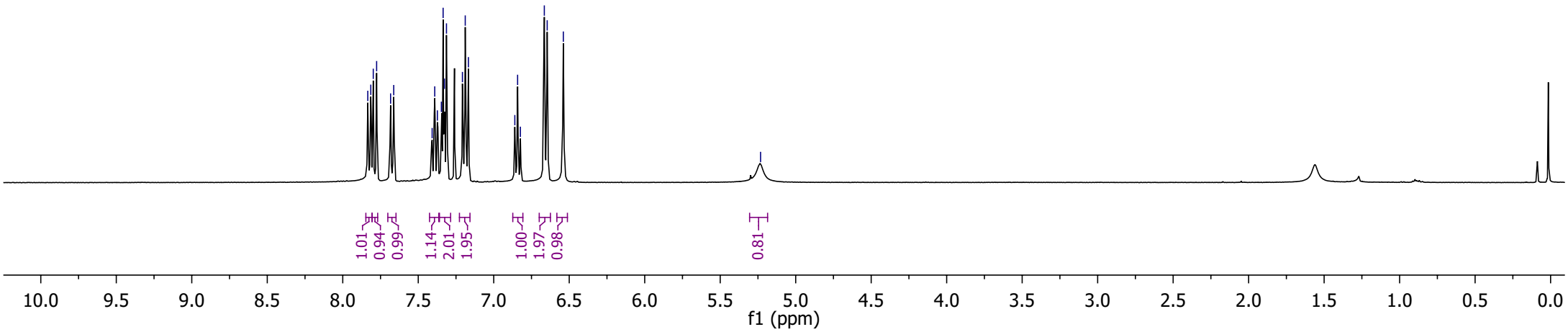
5.233


NH
OH

6a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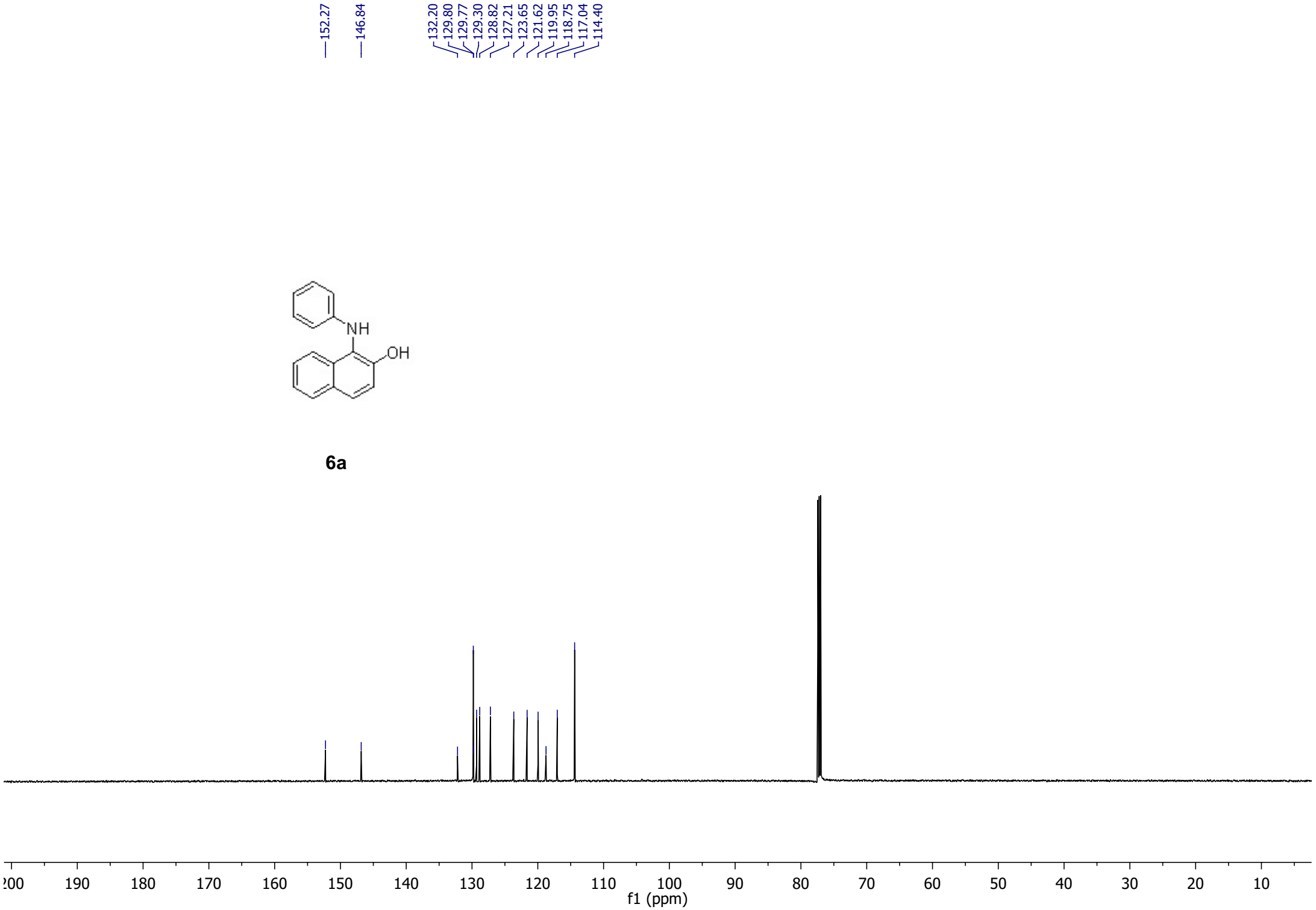
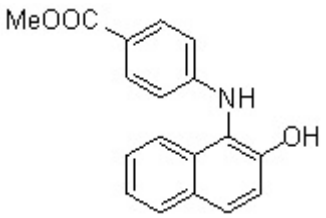
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

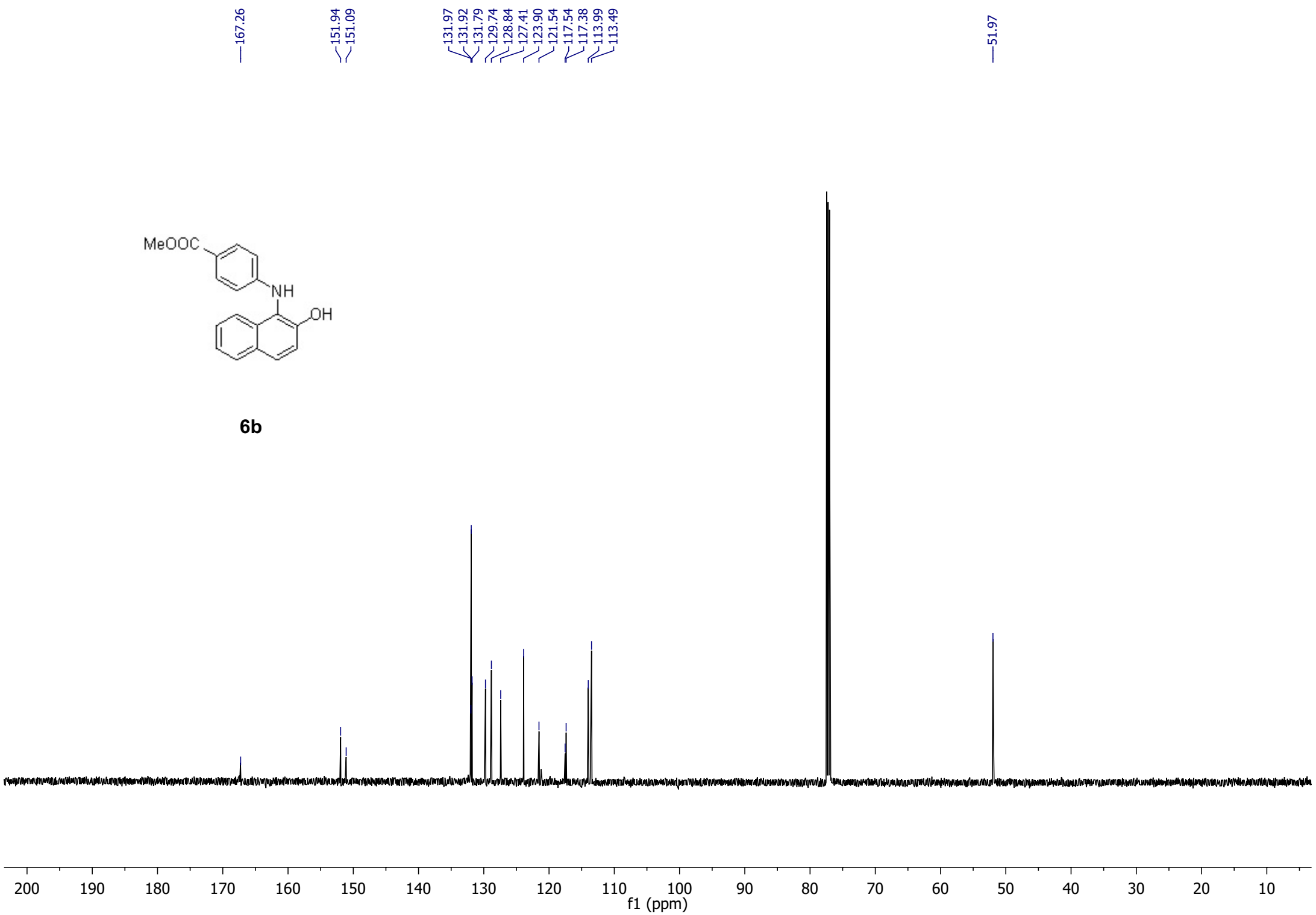

152.27
146.84
132.20
129.80
129.77
129.30
128.82
127.21
123.65
121.62
119.95
118.75
117.04
114.40
NH
OH
f1 (ppm)

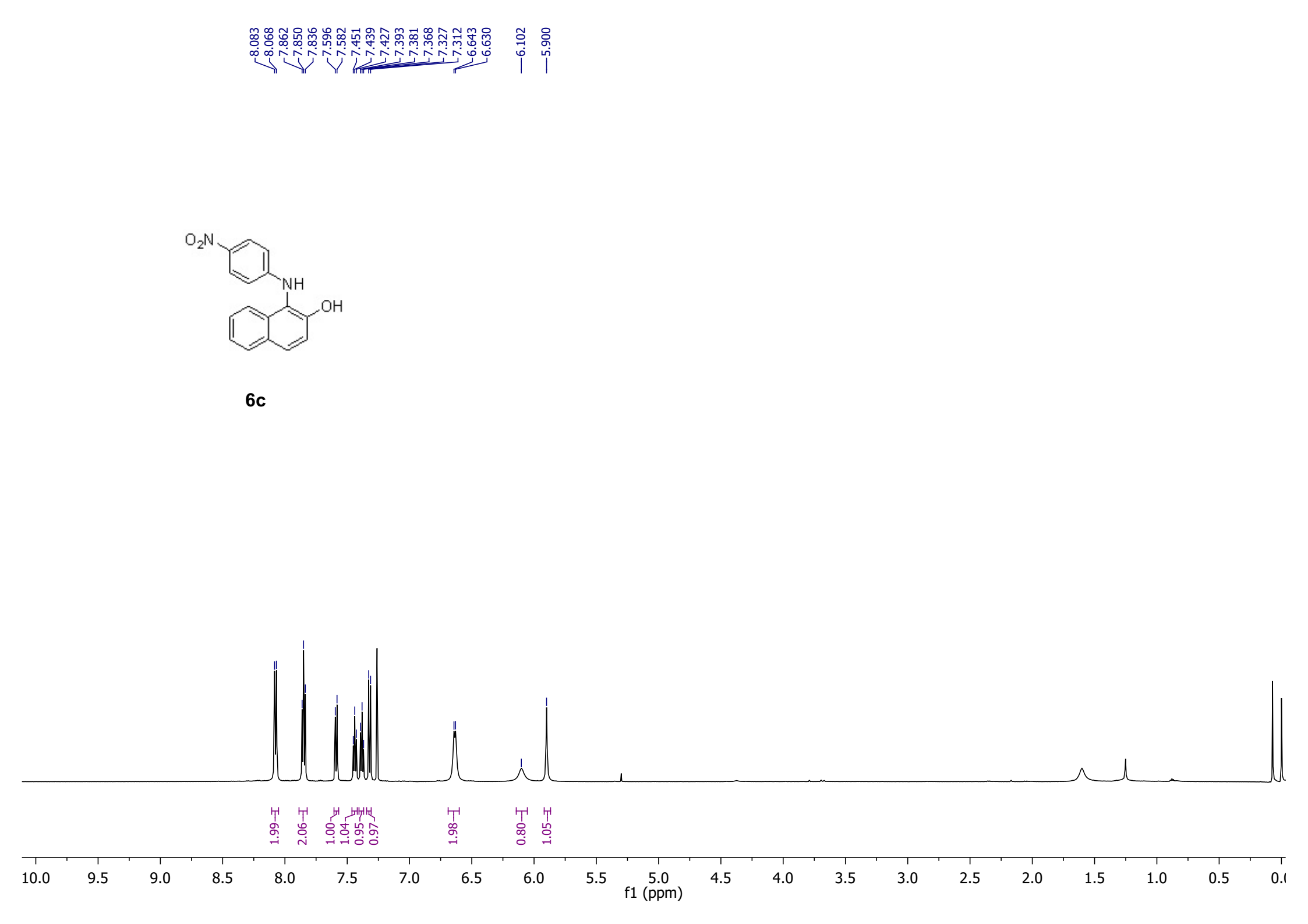
6a


MeOOC
NH
OH

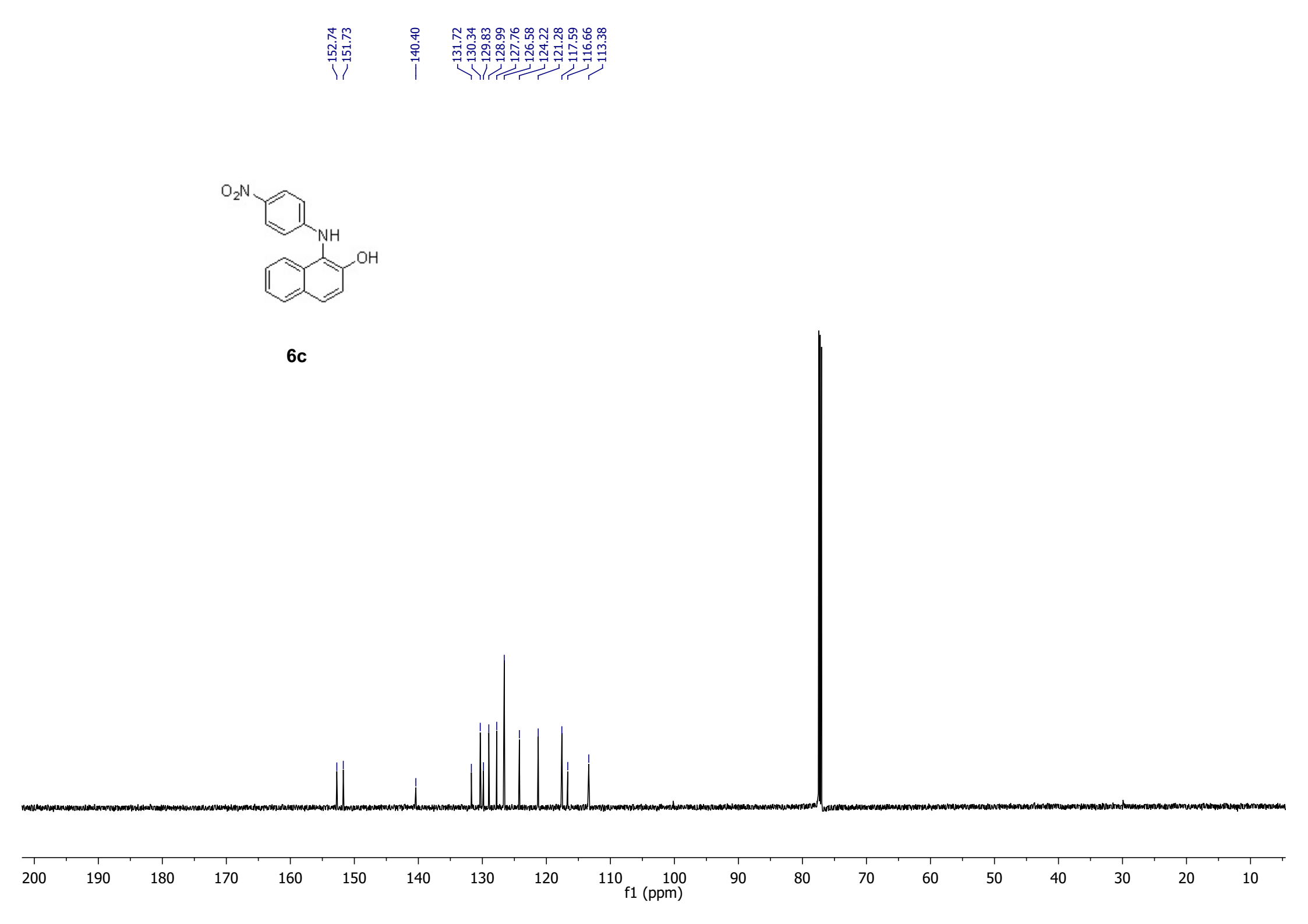
6b

7.854
7.850
7.835
7.822
7.810
7.795
7.618
7.604
7.405
7.393
7.380
7.354
7.343
7.330
7.322
7.307
6.634
6.618
6.602
6.417
5.643
3.836
3.35
1.02
1.00
1.04
1.06
0.96
2.33
0.87
1.01
3.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

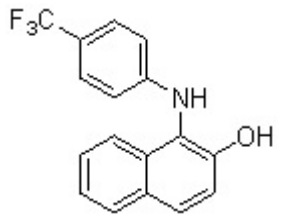

167.26
151.94
151.09
131.97
131.92
131.79
129.74
128.84
127.41
123.90
121.54
117.54
117.38
113.99
113.49
51.97
MeOOC
NH
OH
6b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.083
8.068
7.862
7.850
7.836
7.596
7.582
7.451
7.439
7.427
7.393
7.381
7.368
7.327
7.312
6.643
6.630
6.102
5.900
O2N
NH
OH
1.99
2.06
1.00
1.04
0.95
0.97
1.98
0.80
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

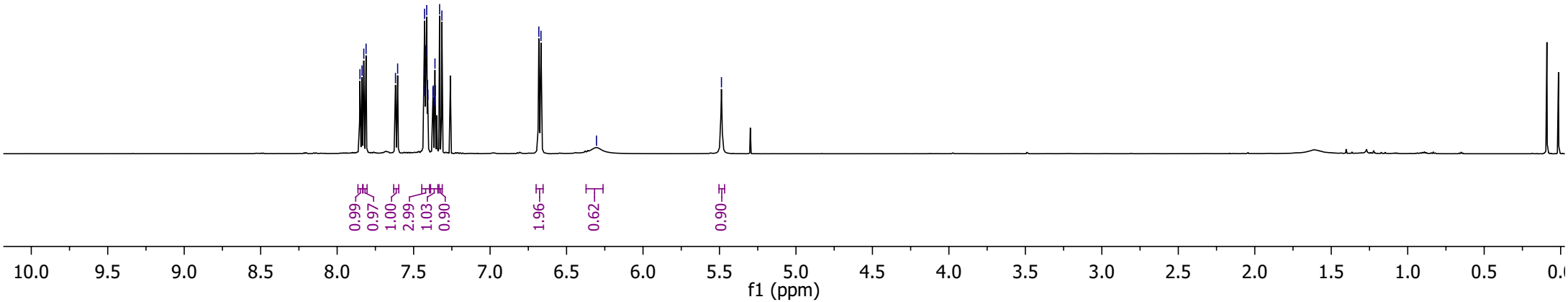
6c

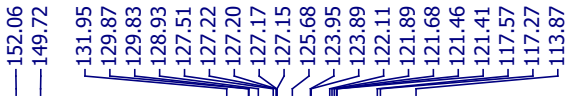

152.74
151.73
140.40
131.72
130.34
129.83
128.99
127.76
126.58
124.22
121.28
117.59
116.66
113.38
O2N
NH
OH
6c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

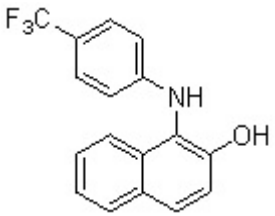

7.851
7.837
7.826
7.811
7.619
7.604
7.434
7.429
7.422
7.420
7.414
7.409
7.406
7.374
7.372
7.362
7.360
7.358
7.330
7.315
6.681
6.667
6.304
5.487


F3C
NH
OH

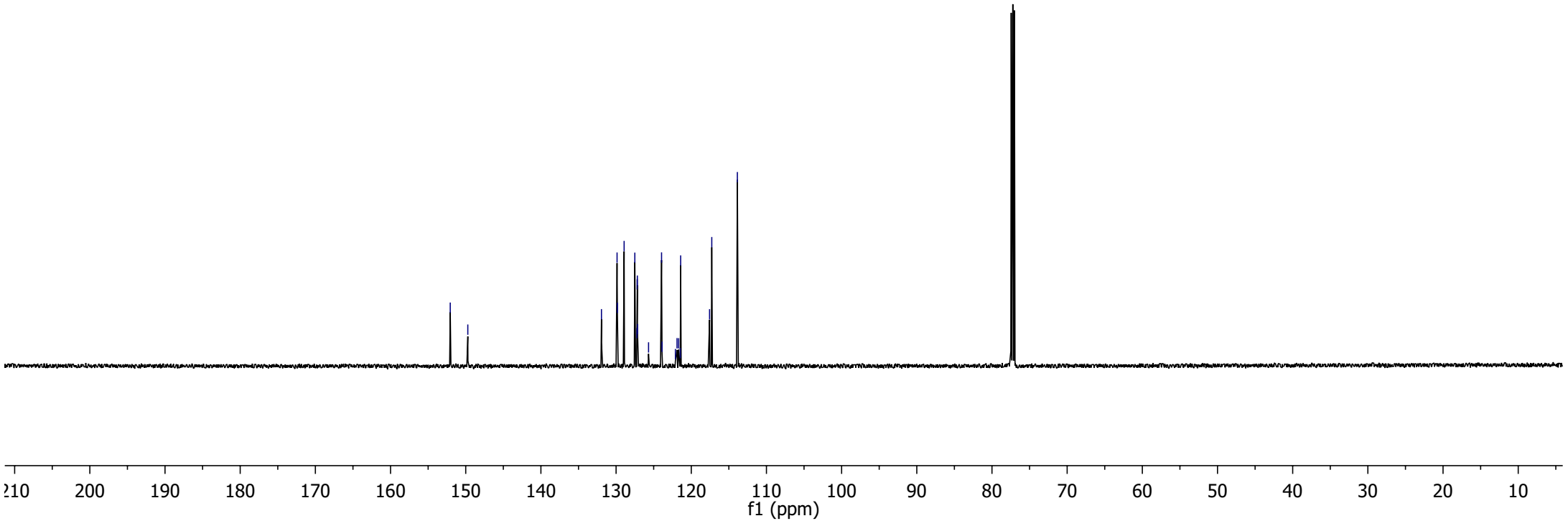
6d


0.99
0.97
1.00
2.99
1.03
0.90
1.96
0.62
0.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

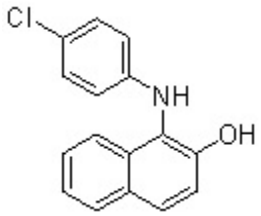

152.06
149.72
131.95
129.87
129.83
128.93
127.51
127.22
127.20
127.17
127.15
125.68
123.95
123.89
122.11
121.89
121.68
121.46
121.41
117.57
117.27
113.87


F3C
NH
OH

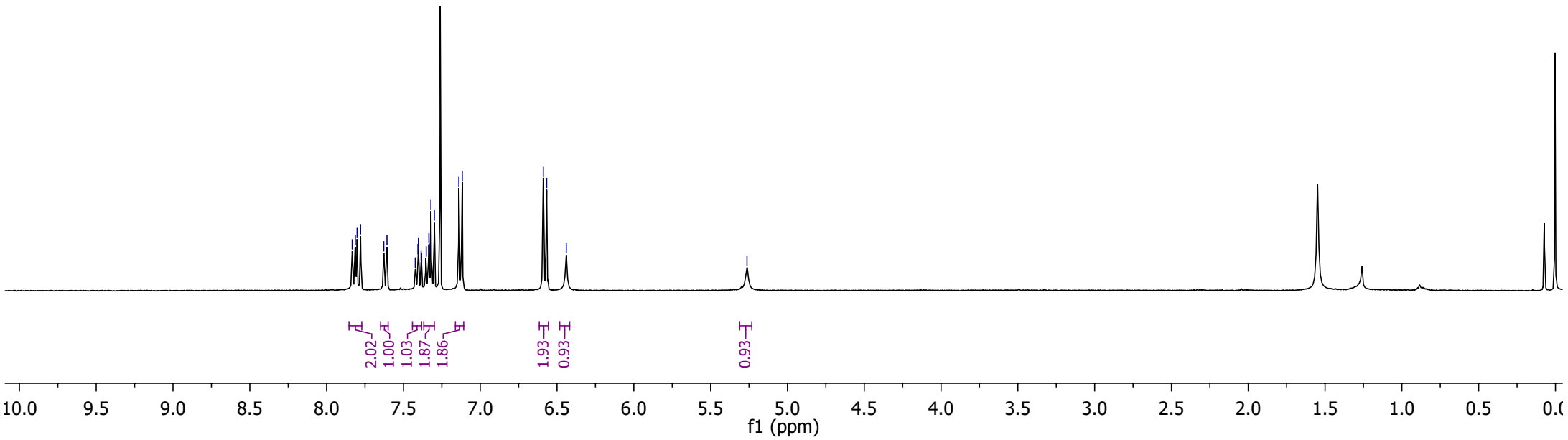
6d

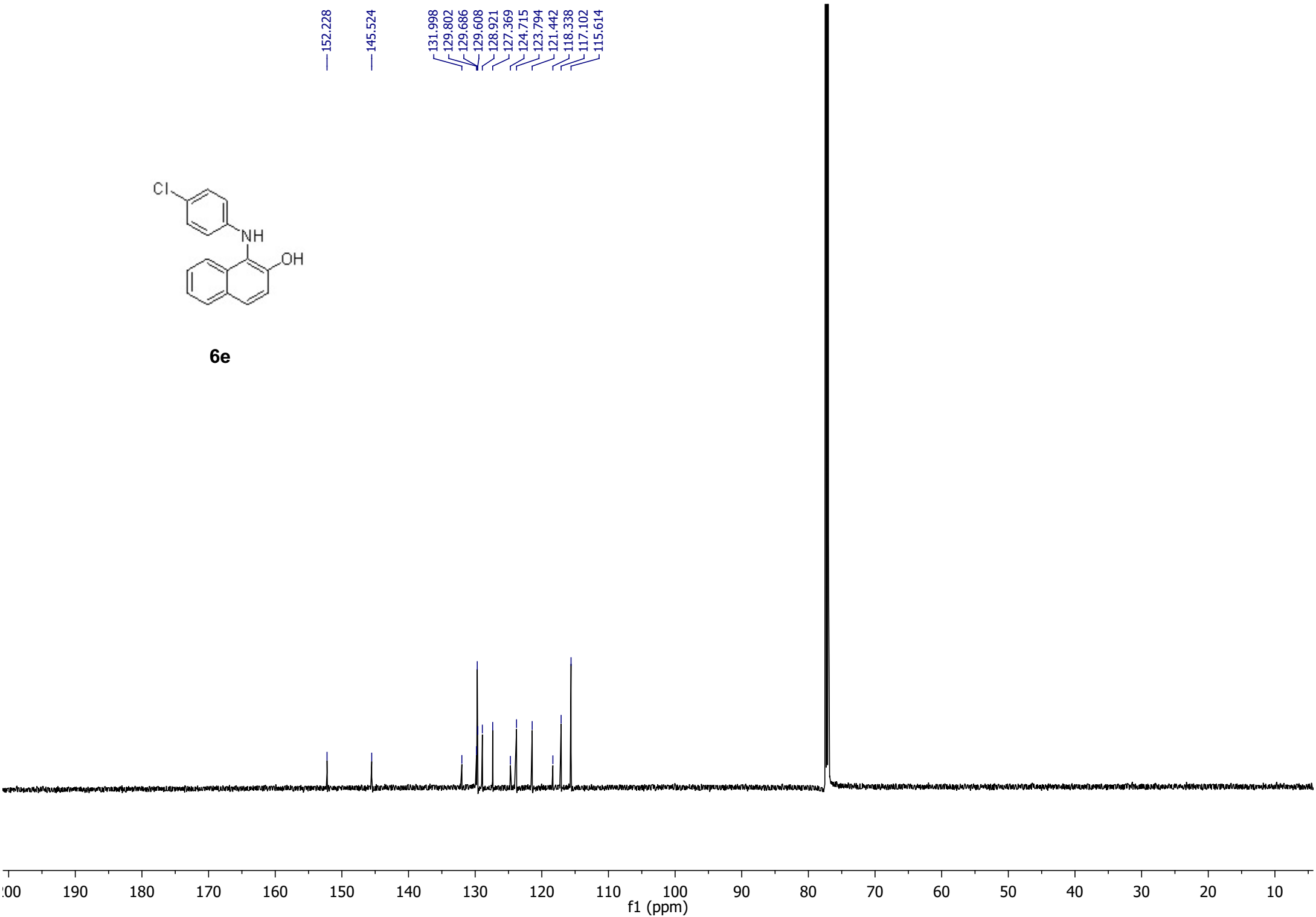

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.833
7.813
7.801
7.779
7.628
7.607
7.423
7.420
7.406
7.402
7.385
7.382
7.351
7.334
7.332
7.321
7.299
7.139
7.117
6.589
6.567
6.440
5.263

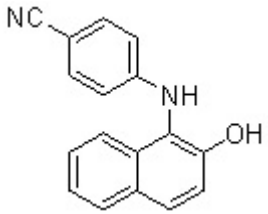

Cl
NH
OH

6e

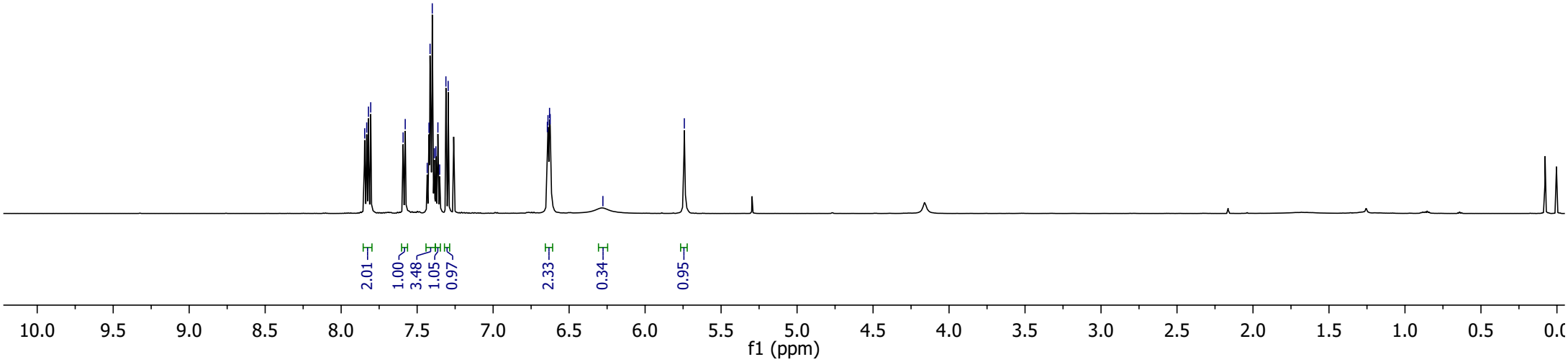

2.02
1.00
1.03
1.87
1.86
1.93
0.93
0.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

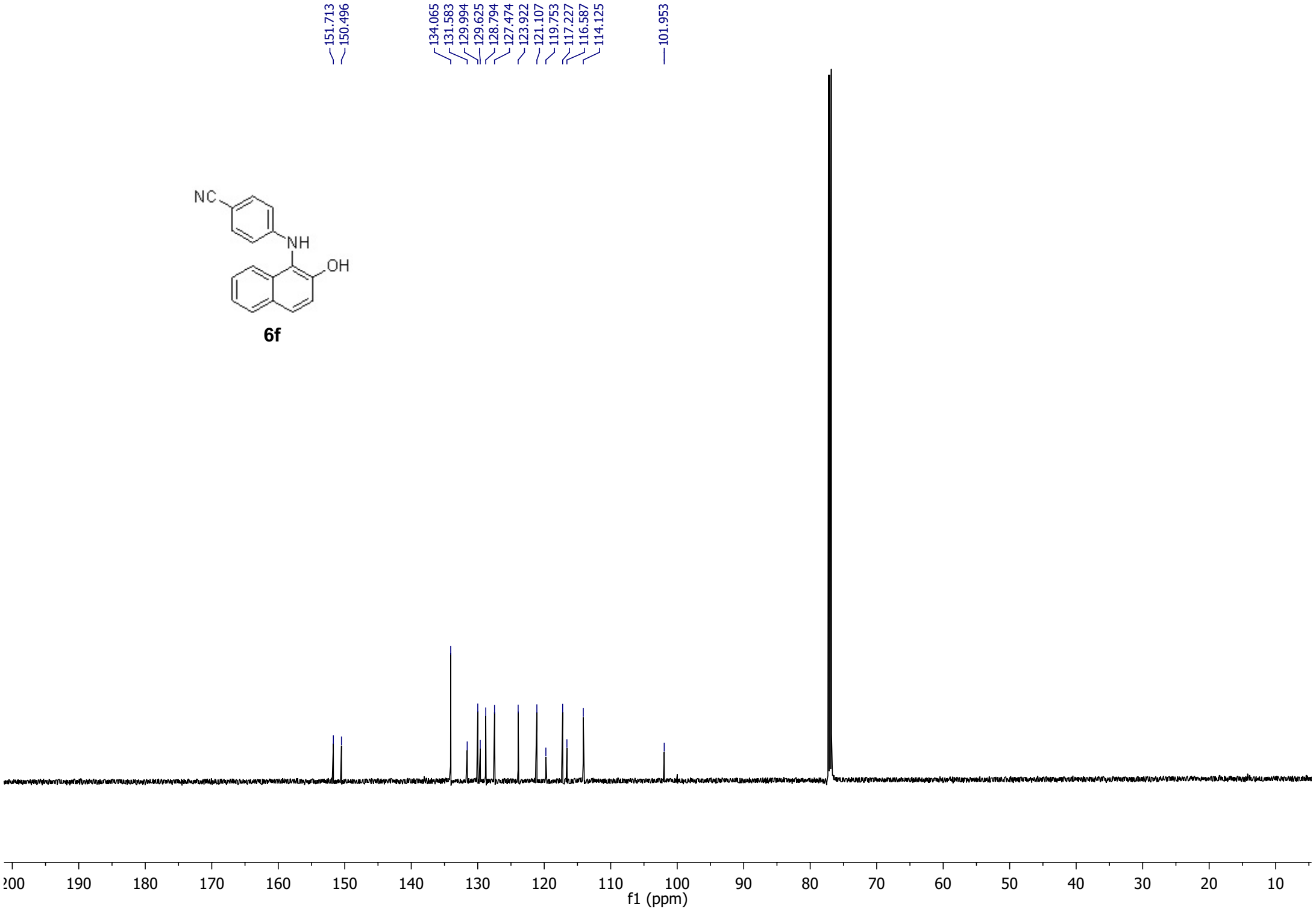

152.228
145.524
131.998
129.802
129.686
129.608
128.921
127.369
124.715
123.794
121.442
118.338
117.102
115.614
Cl
NH
OH
6e
f1 (ppm)


7.845
7.832
7.820
7.805
7.592
7.578
7.434
7.422
7.415
7.400
7.387
7.377
7.363
7.352
7.311
7.296
6.643
6.639
6.629
6.625
6.278
5.742

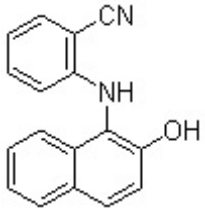

NC
NH
OH

6f

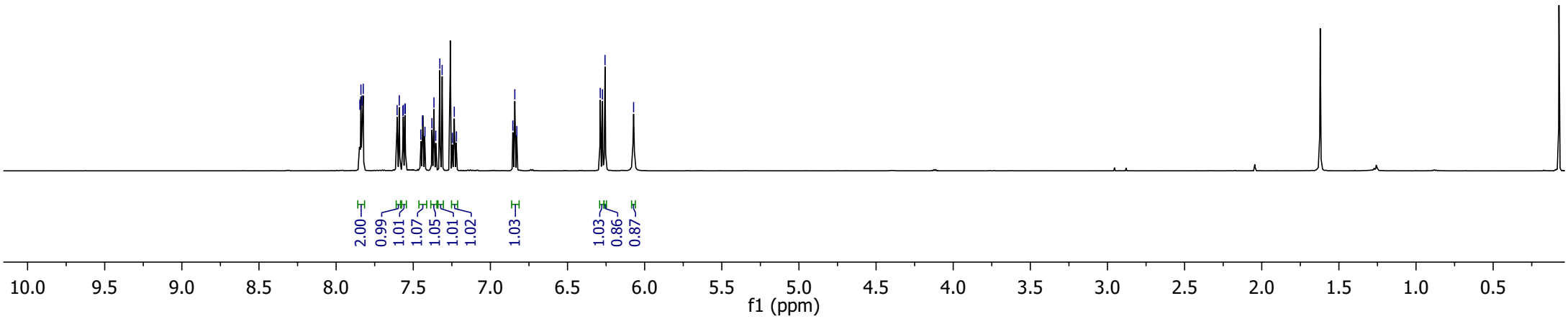

2.01
1.00
3.48
1.05
0.97
2.33
0.34
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

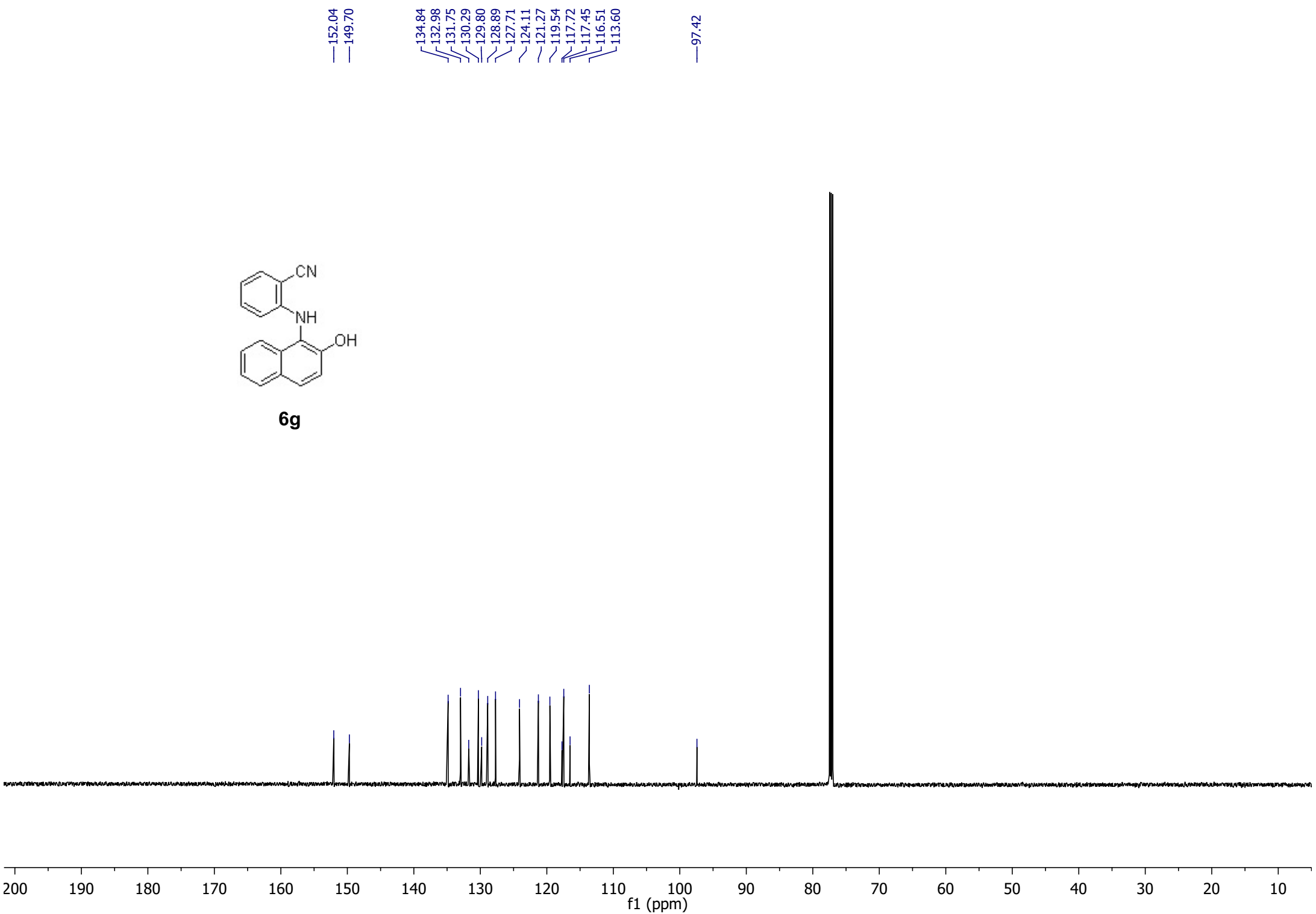

151.713
150.496
134.065
131.583
129.994
129.625
128.794
127.474
123.922
121.107
119.753
117.227
116.587
114.125
101.953
NC
NH
OH
6f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.846
7.839
7.833
7.824
7.605
7.591
7.567
7.565
7.554
7.552
7.451
7.440
7.424
7.379
7.366
7.354
7.328
7.313
7.246
7.234
7.220
6.855
6.842
6.828
6.288
6.274
6.257
6.072

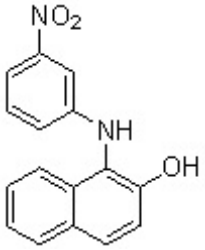

CN
NH
OH

6g

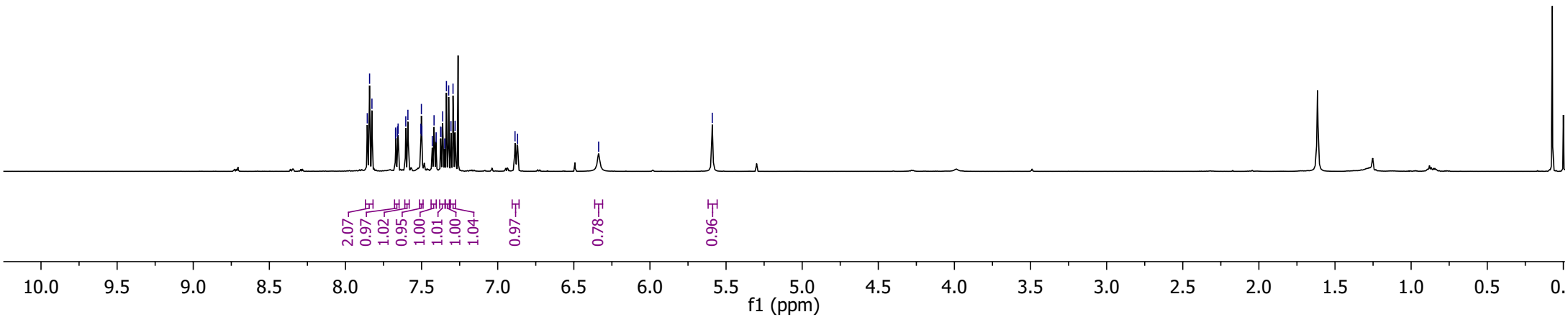

2.00
0.99
1.01
1.07
1.05
1.01
1.02
1.03
1.03
0.86
0.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

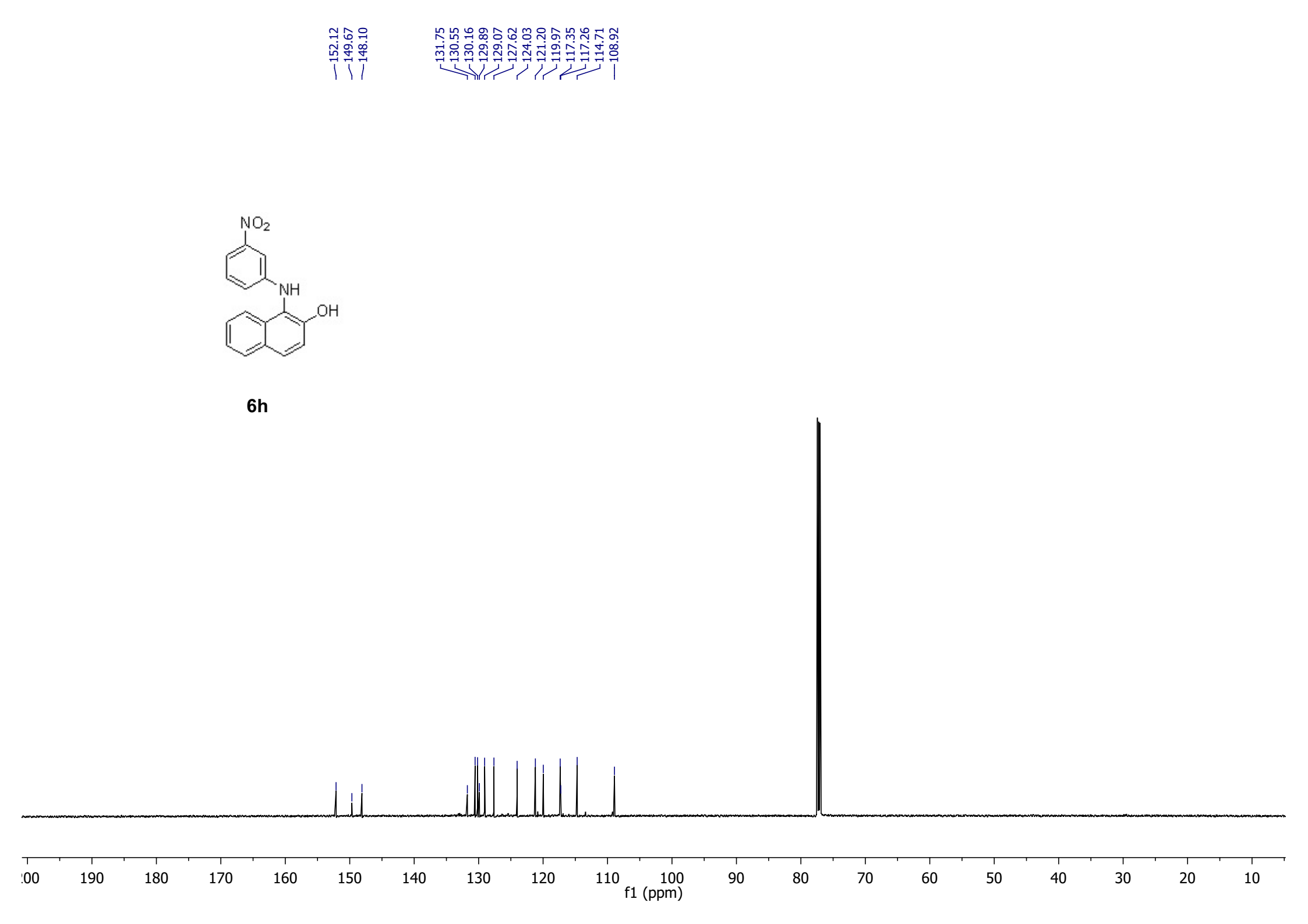

152.04
149.70
134.84
132.98
131.75
130.29
129.80
128.89
127.71
124.11
121.27
119.54
117.72
117.45
116.51
113.60
97.42
CN
NH
OH
6g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.857
7.842
7.826
7.671
7.670
7.658
7.654
7.604
7.590
7.505
7.501
7.498
7.430
7.418
7.404
7.375
7.373
7.361
7.348
7.337
7.322
7.307
7.294
7.280
6.886
6.870
6.337
5.591

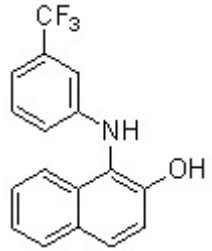

NO2
NH
OH

6h

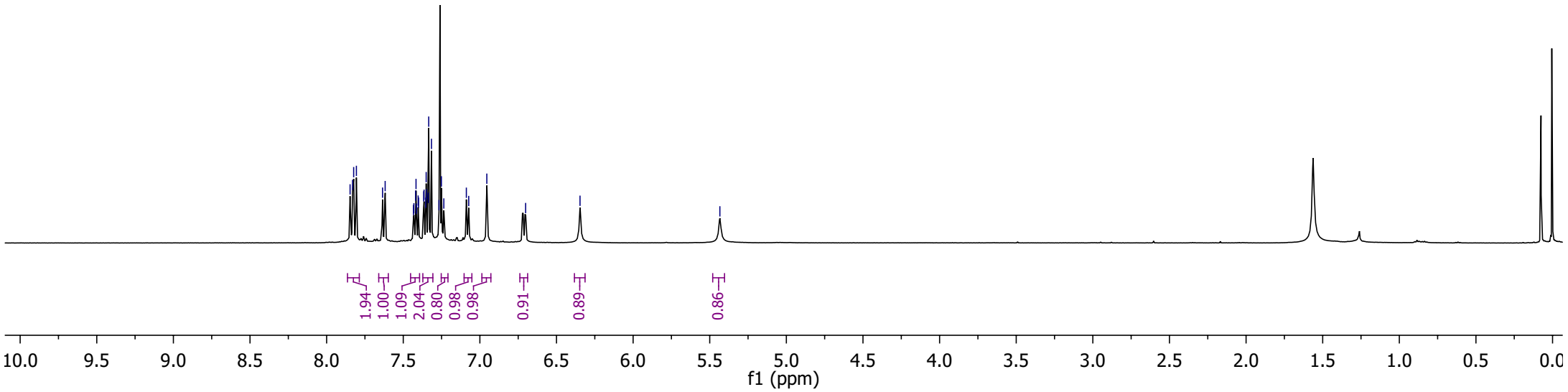

2.07
0.97
1.02
0.95
1.00
1.01
1.00
1.04
0.97
0.78
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

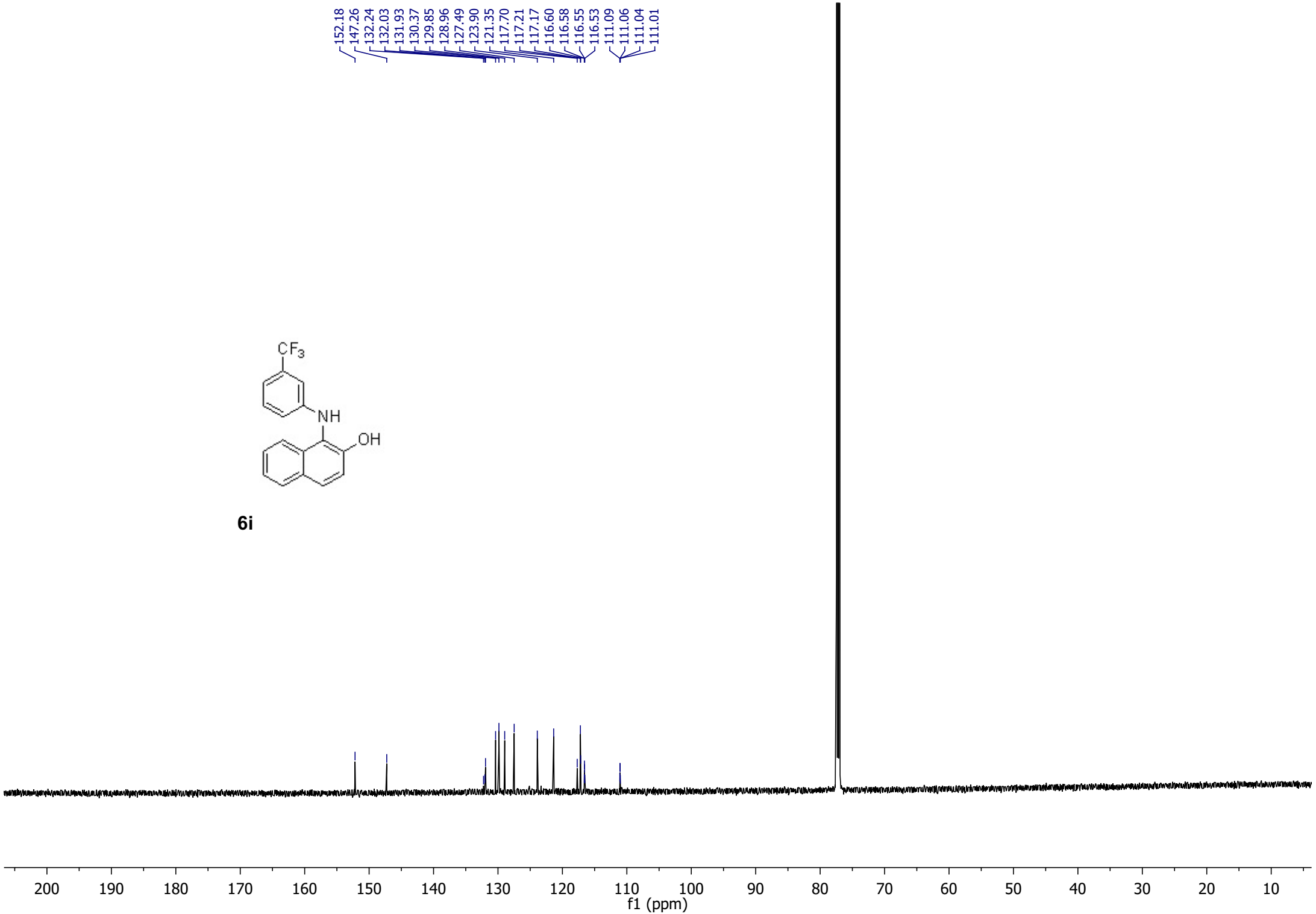

152.12
149.67
148.10
131.75
130.55
130.16
129.89
129.07
127.62
124.03
121.20
119.97
117.35
117.26
114.71
108.92
NO2
NH
OH
6h
f1 (ppm)

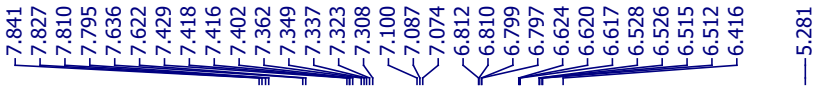

7.847
7.831
7.824
7.806
7.635
7.618
7.433
7.431
7.419
7.417
7.414
7.403
7.400
7.367
7.364
7.353
7.350
7.348
7.336
7.334
7.316
7.267
7.251
7.235
7.088
7.073
6.955
6.701
6.347
5.434

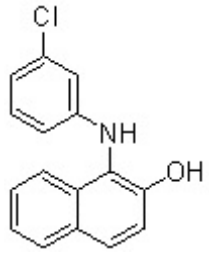

CF3
NH
OH

6i

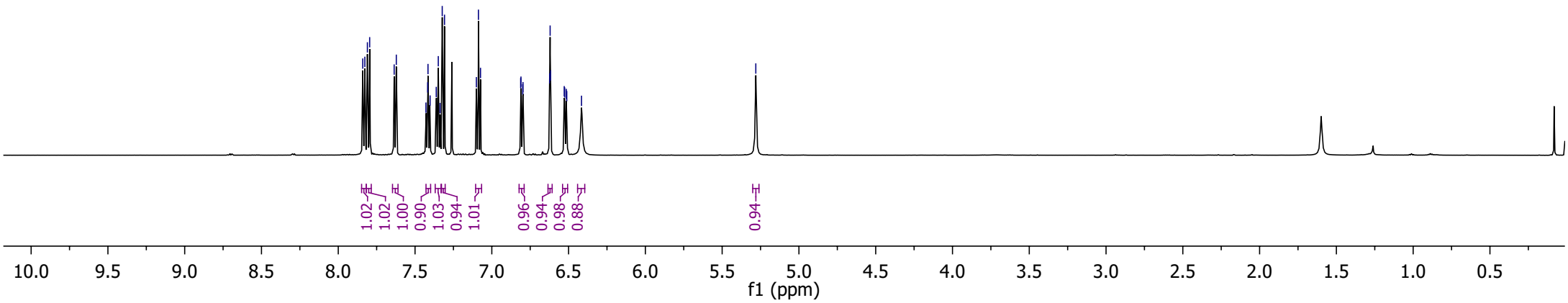

1.94
1.00
1.09
2.04
0.80
0.98
0.98
0.91
0.89
0.86
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

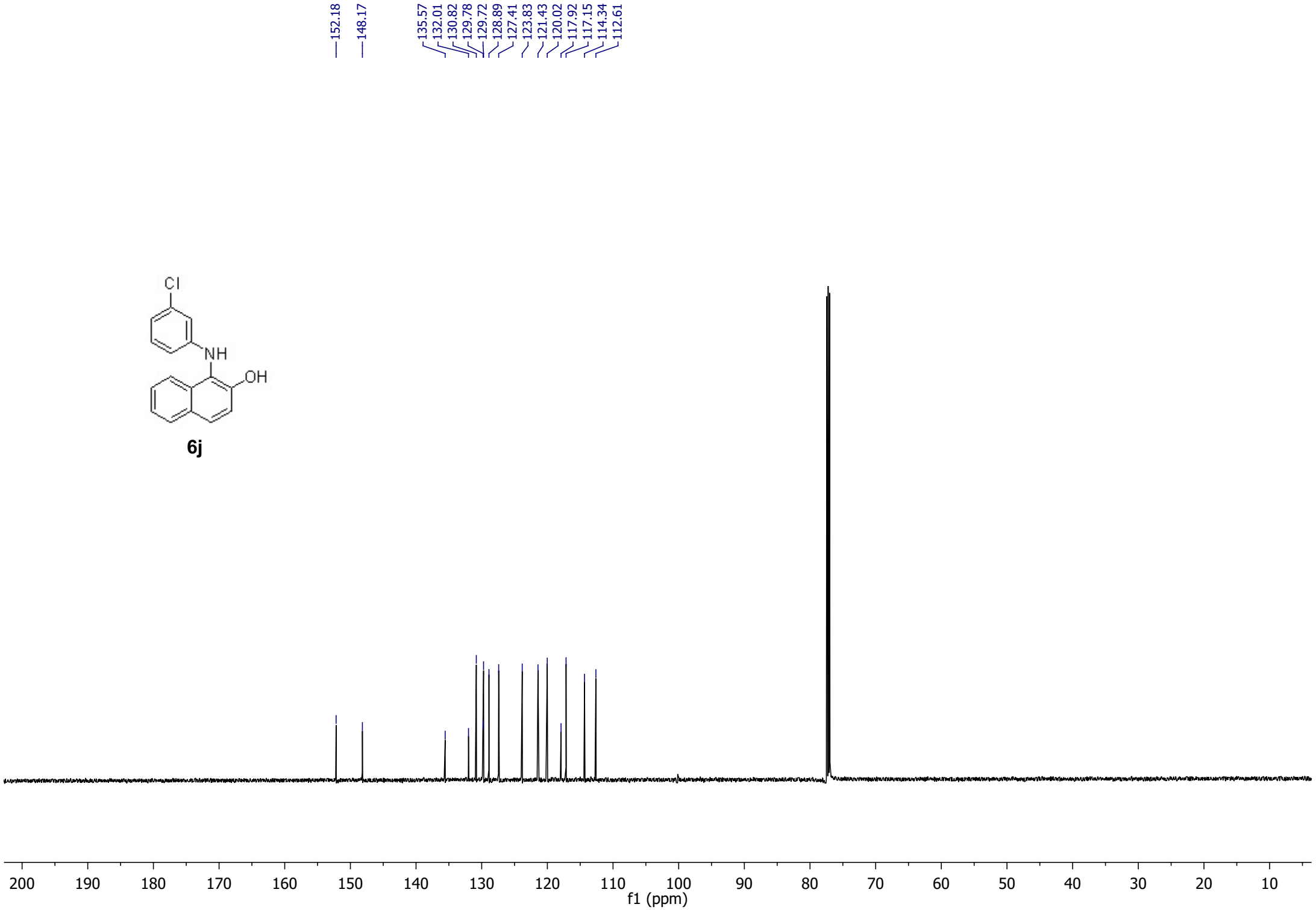

152.18
147.26
132.24
132.03
131.93
130.37
129.85
128.96
127.49
123.90
121.35
117.70
117.21
117.17
116.60
116.58
116.55
116.53
111.09
111.06
111.04
111.01
CF3
NH
OH
6i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

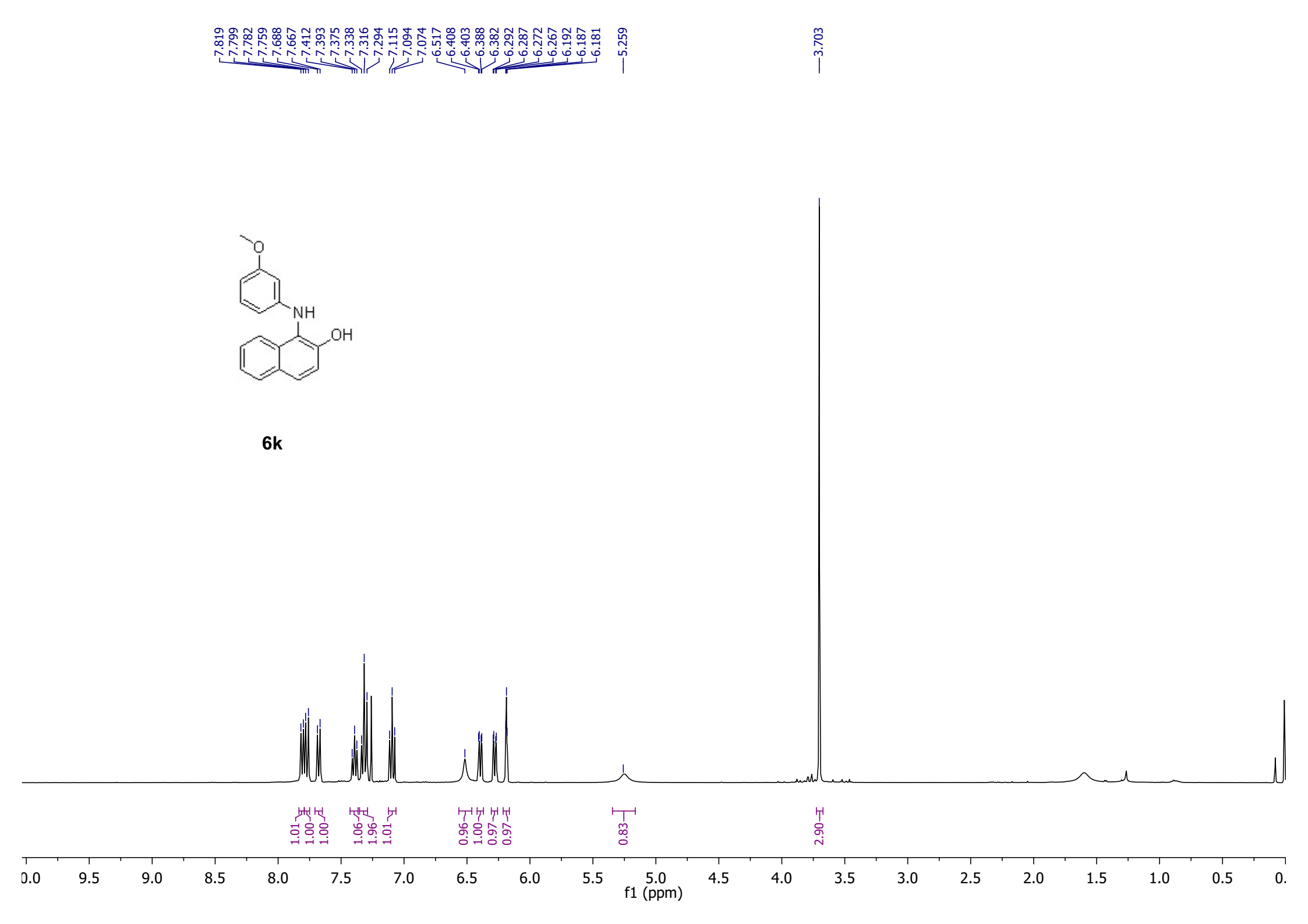

7.841
7.827
7.810
7.795
7.636
7.622
7.429
7.418
7.416
7.402
7.362
7.349
7.337
7.323
7.308
7.100
7.087
7.074
6.812
6.810
6.799
6.797
6.624
6.620
6.617
6.528
6.526
6.515
6.512
6.416
5.281

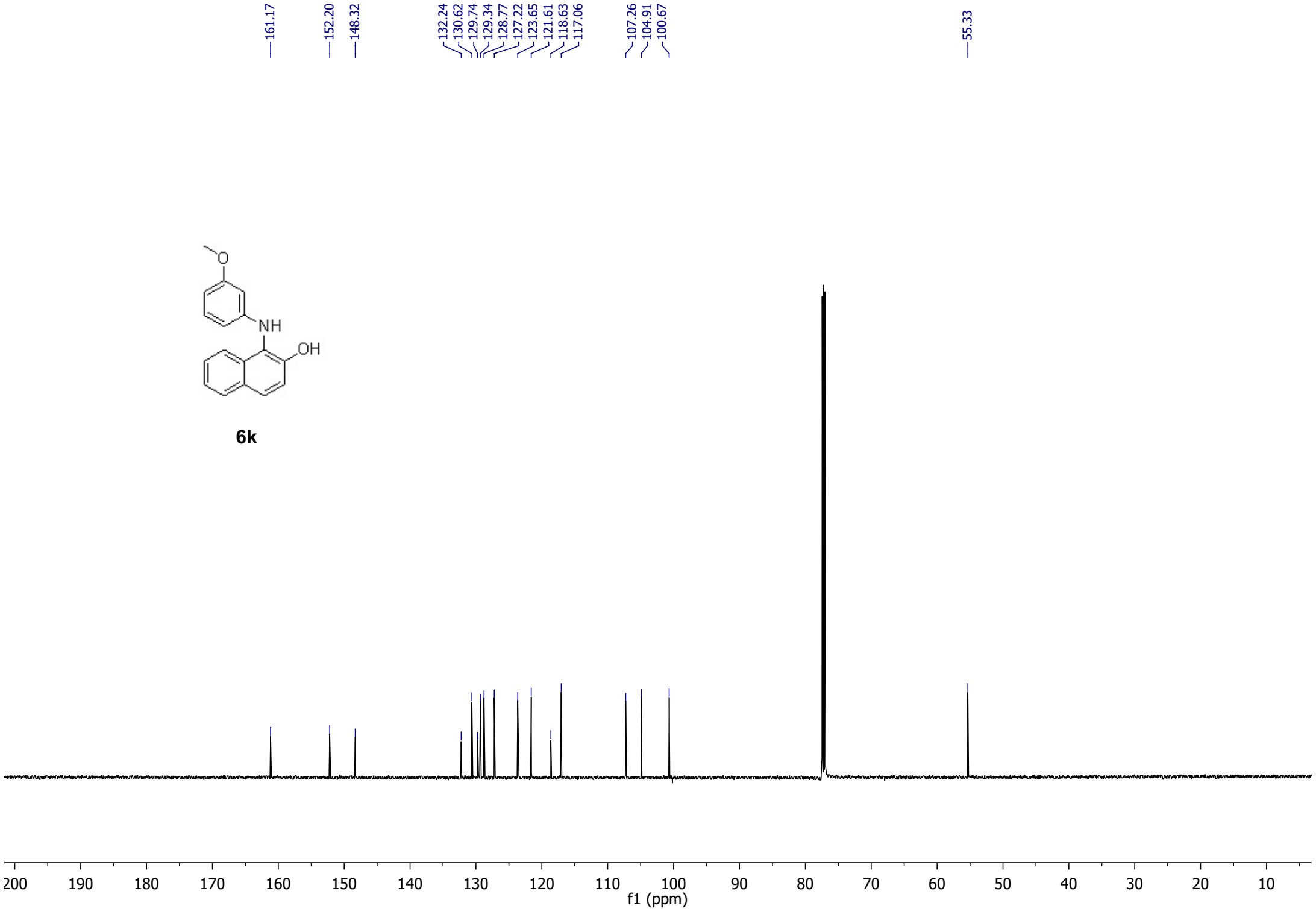

Cl
NH
OH

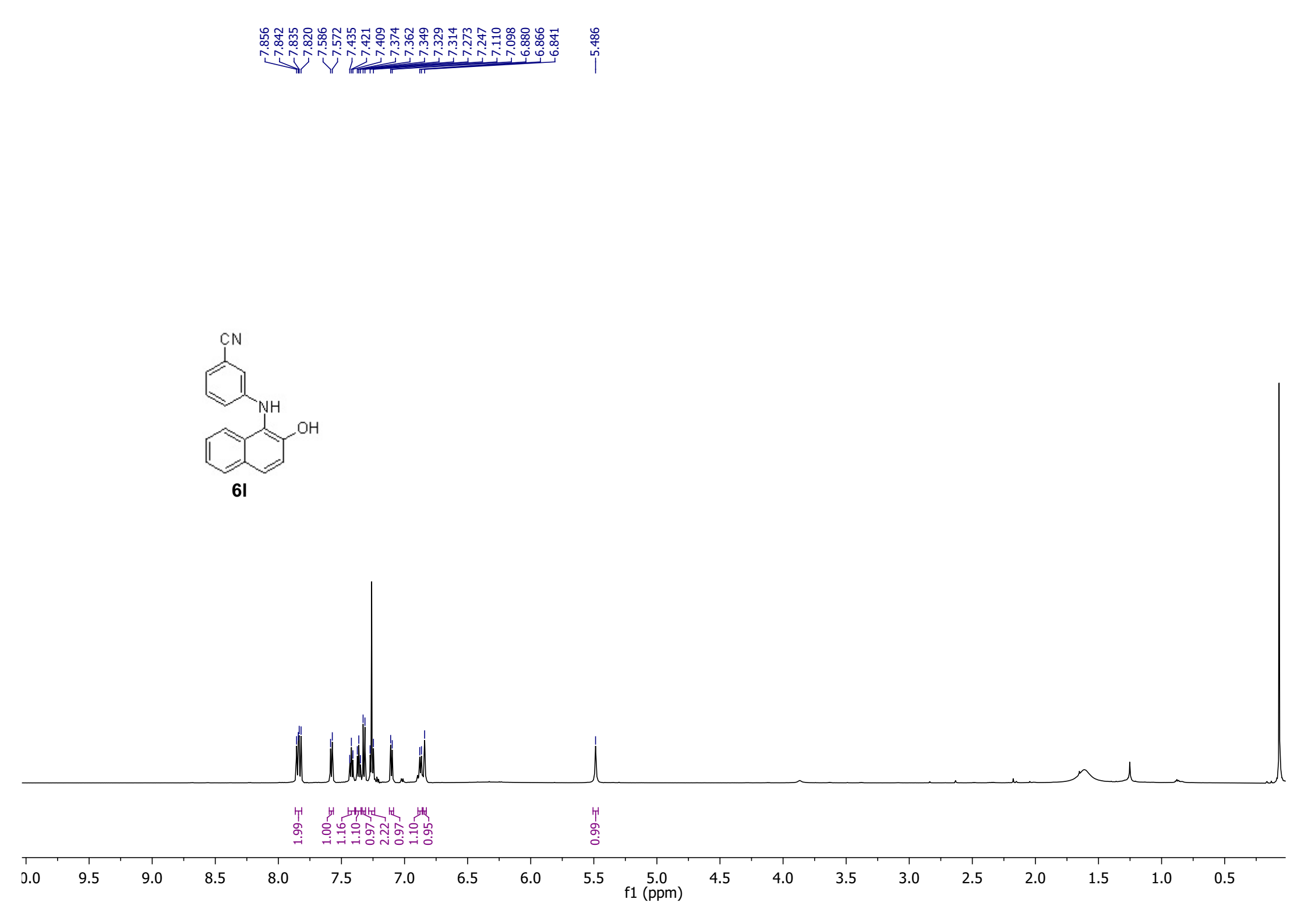
6j

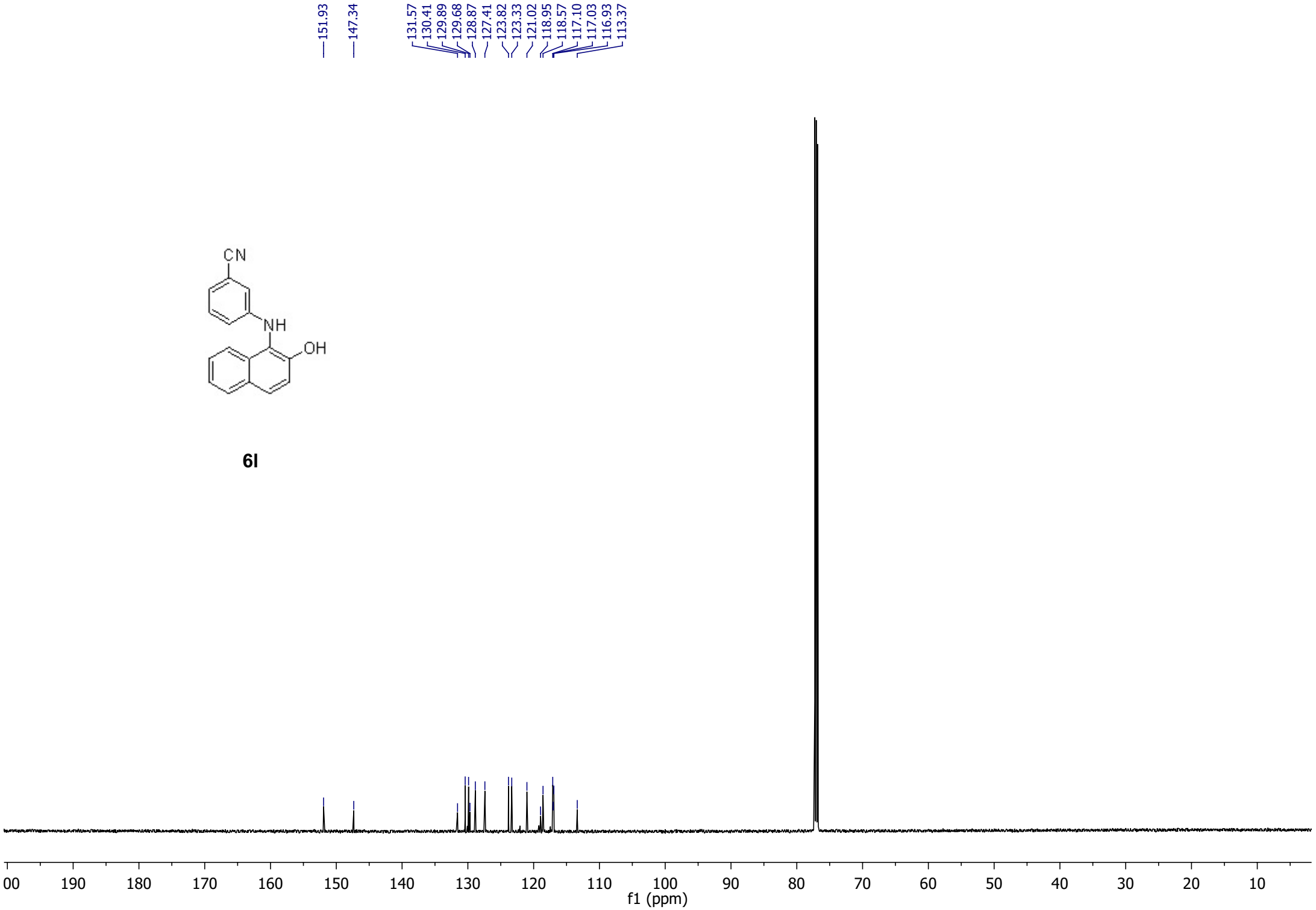

1.02
1.02
1.00
0.90
1.03
0.94
1.01
0.96
0.94
0.98
0.88
0.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


152.18
148.17
135.57
132.01
130.82
129.78
129.72
128.89
127.41
123.83
121.43
120.02
117.92
117.15
114.34
112.61
Cl
NH
OH
6j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

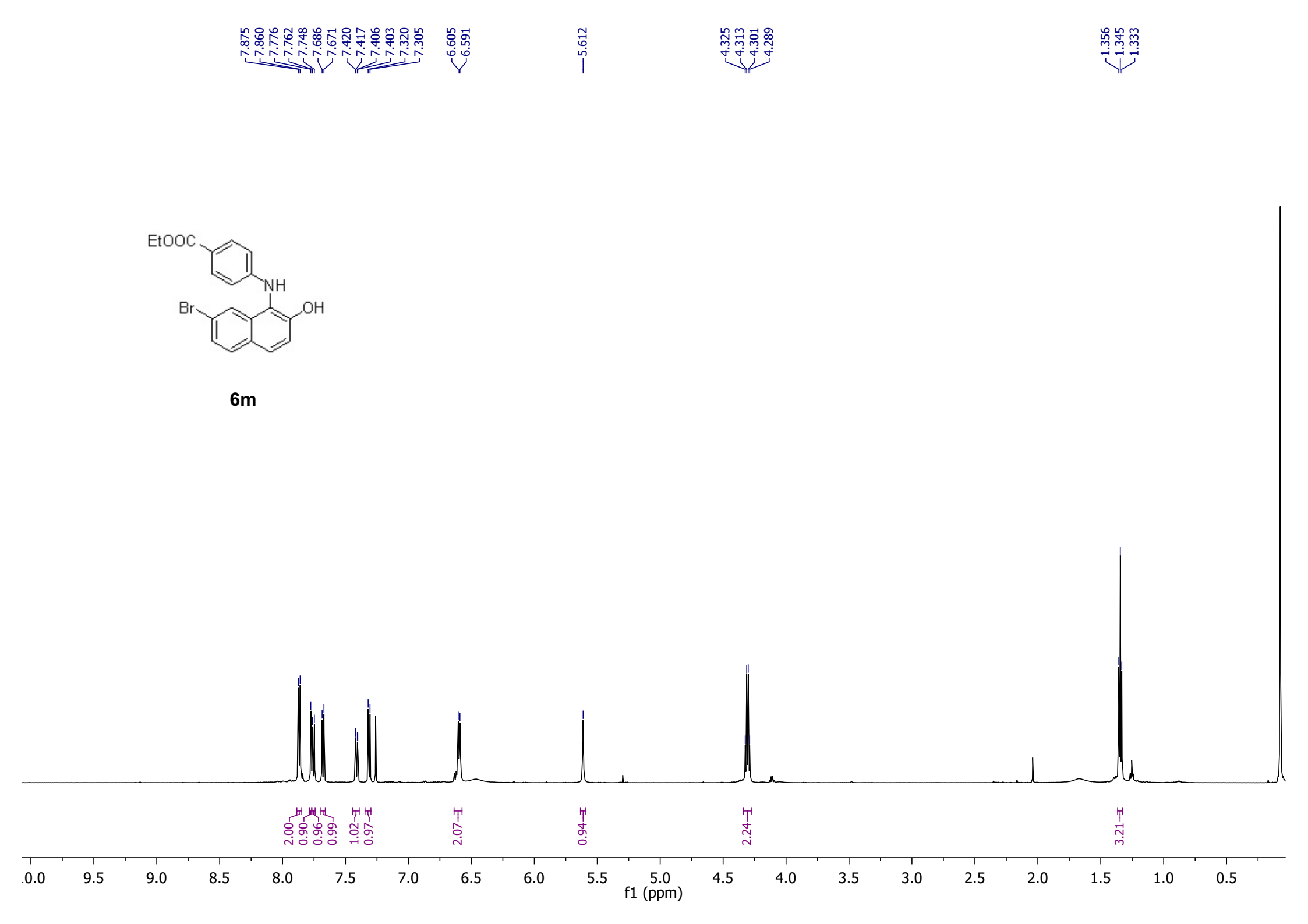

7.819
7.799
7.782
7.759
7.688
7.667
7.412
7.393
7.375
7.338
7.316
7.294
7.115
7.094
7.074
6.517
6.408
6.403
6.388
6.382
6.292
6.287
6.272
6.267
6.192
6.187
6.181
5.259
3.703
O
NH
OH
6k
1.01
1.00
1.00
1.06
1.96
1.01
0.96
1.00
0.97
0.97
0.83
2.90
f1 (ppm)


161.17
152.20
148.32
132.24
130.62
129.74
129.34
128.77
127.22
123.65
121.61
118.63
117.06
107.26
104.91
100.67
55.33
O
NH
OH
6k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

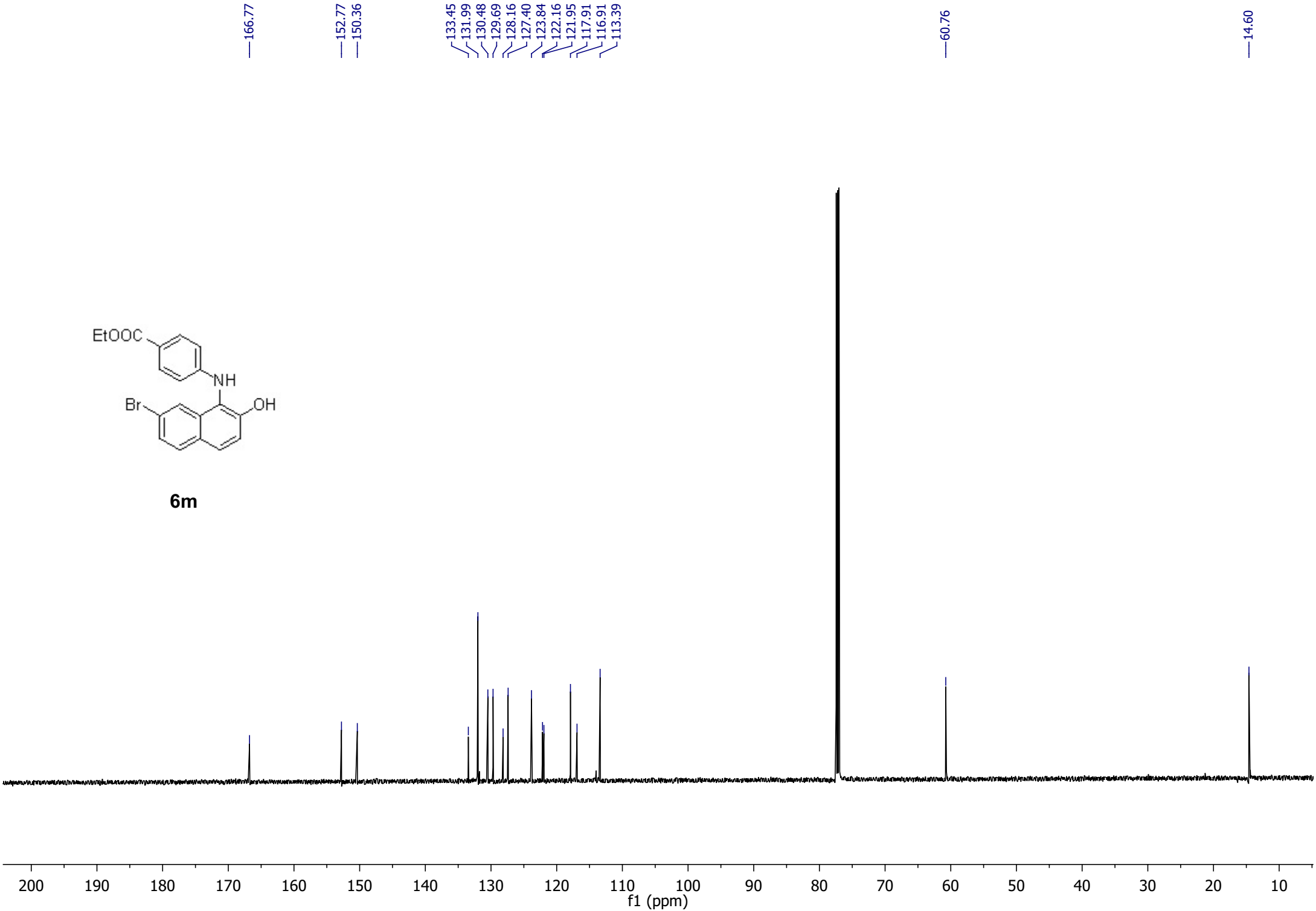

7.856
7.842
7.835
7.820
7.586
7.572
7.435
7.421
7.409
7.374
7.362
7.349
7.329
7.314
7.273
7.247
7.110
7.098
6.880
6.866
6.841
5.486
CN
NH
OH
6l
1.99
1.00
1.16
1.10
0.97
2.22
0.97
1.10
0.95
0.99
f1 (ppm)

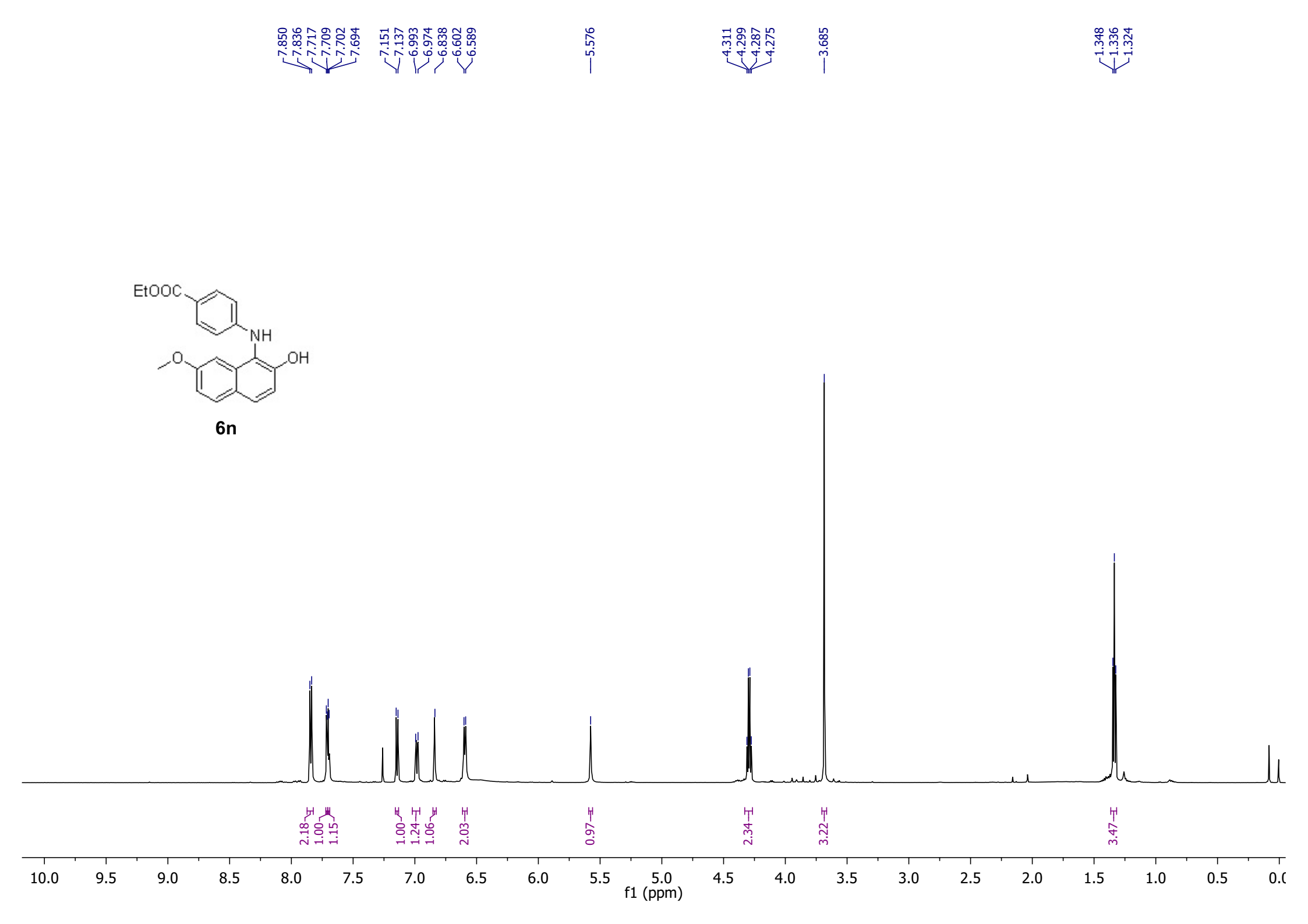

151.93
147.34
131.57
130.41
129.89
129.68
128.87
127.41
123.82
123.33
121.02
118.95
118.57
117.10
117.03
116.93
113.37
CN
NH
OH
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

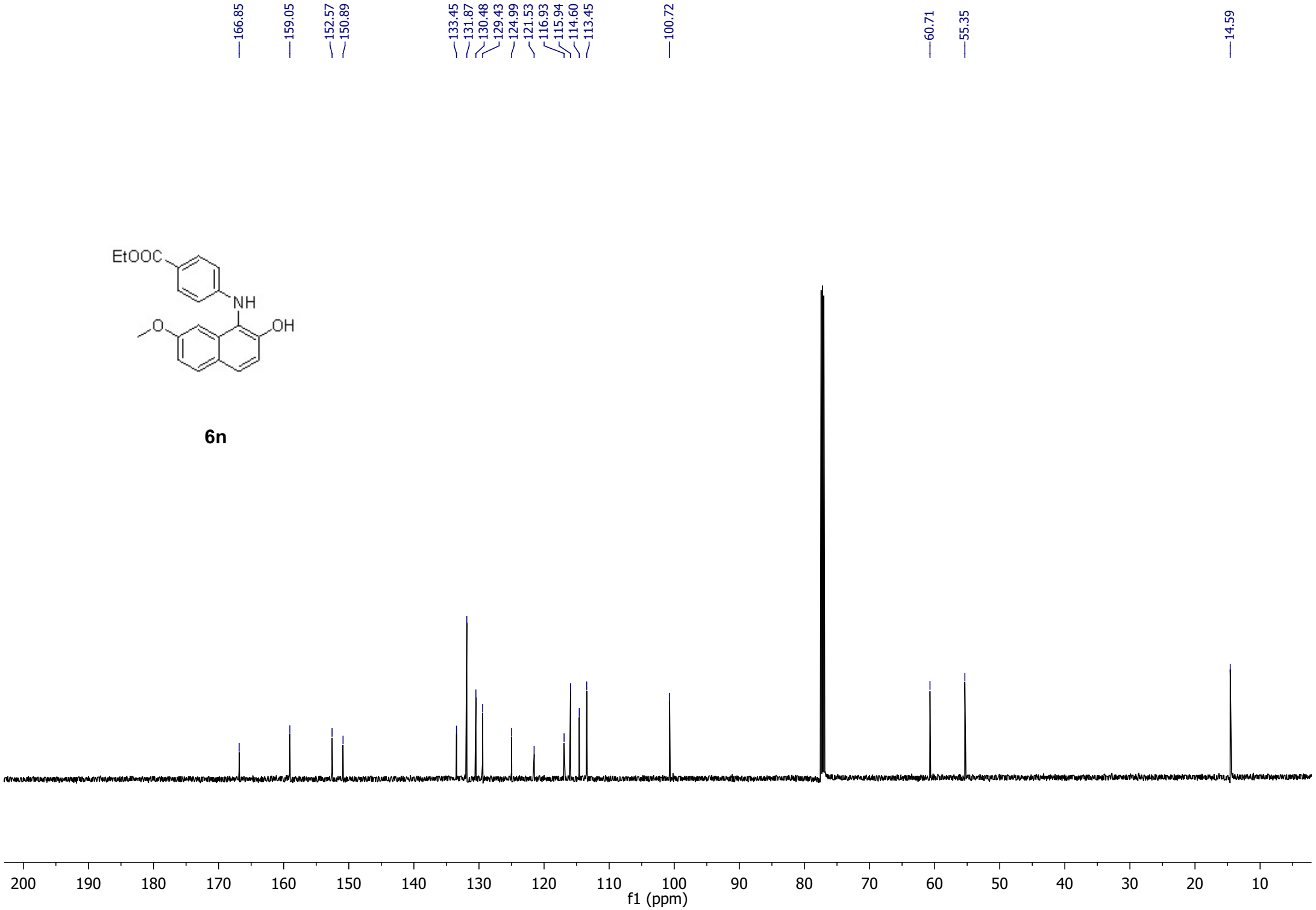
6l

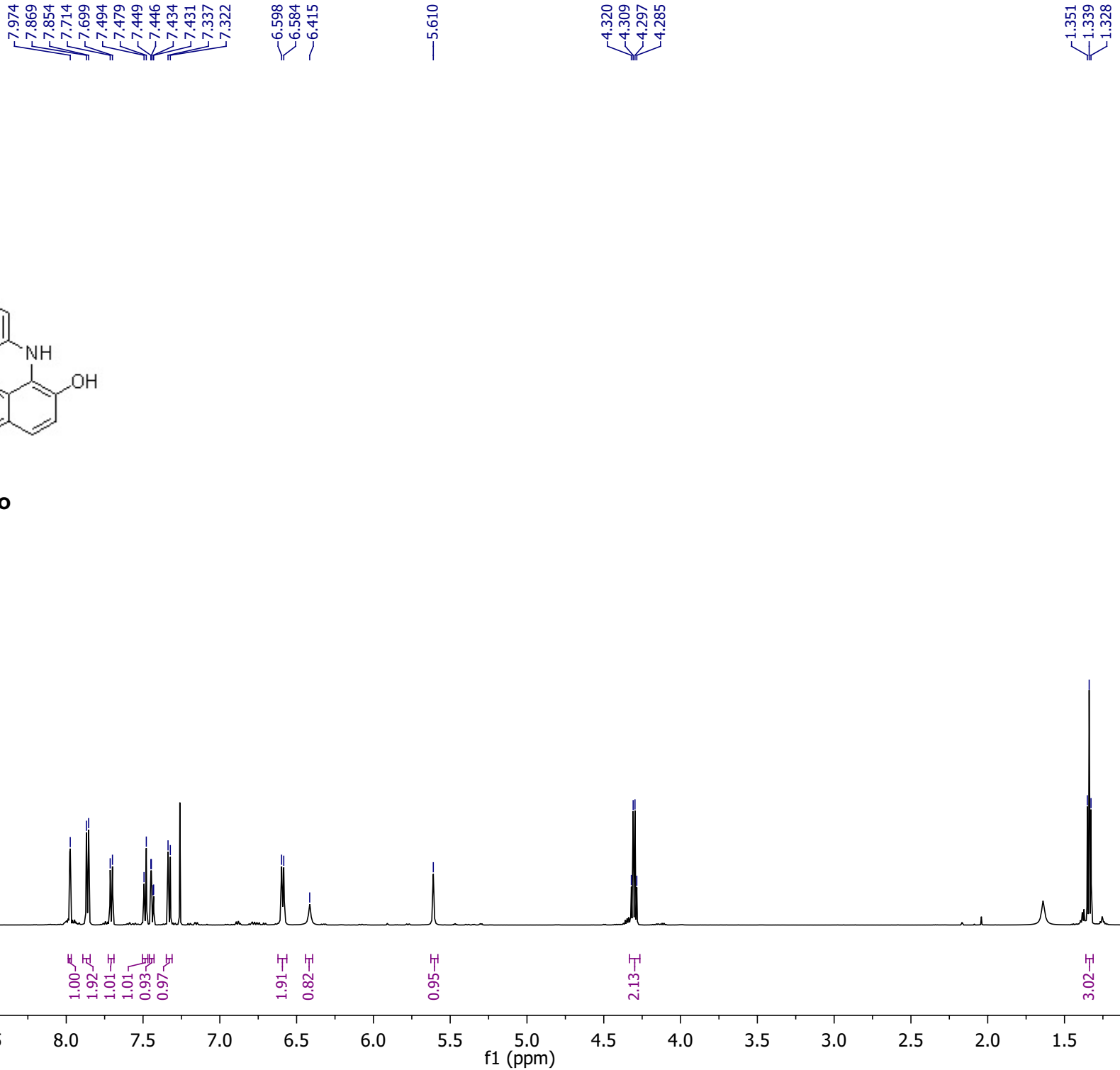

7.875
7.860
7.776
7.762
7.748
7.686
7.671
7.420
7.417
7.406
7.403
7.320
7.305
6.605
6.591
5.612
4.325
4.313
4.301
4.289
1.356
1.345
1.333
EtOOC
NH
Br
OH
2.00
0.90
0.96
0.99
1.02
0.97
2.07
0.94
2.24
3.21
f1 (ppm)

6m

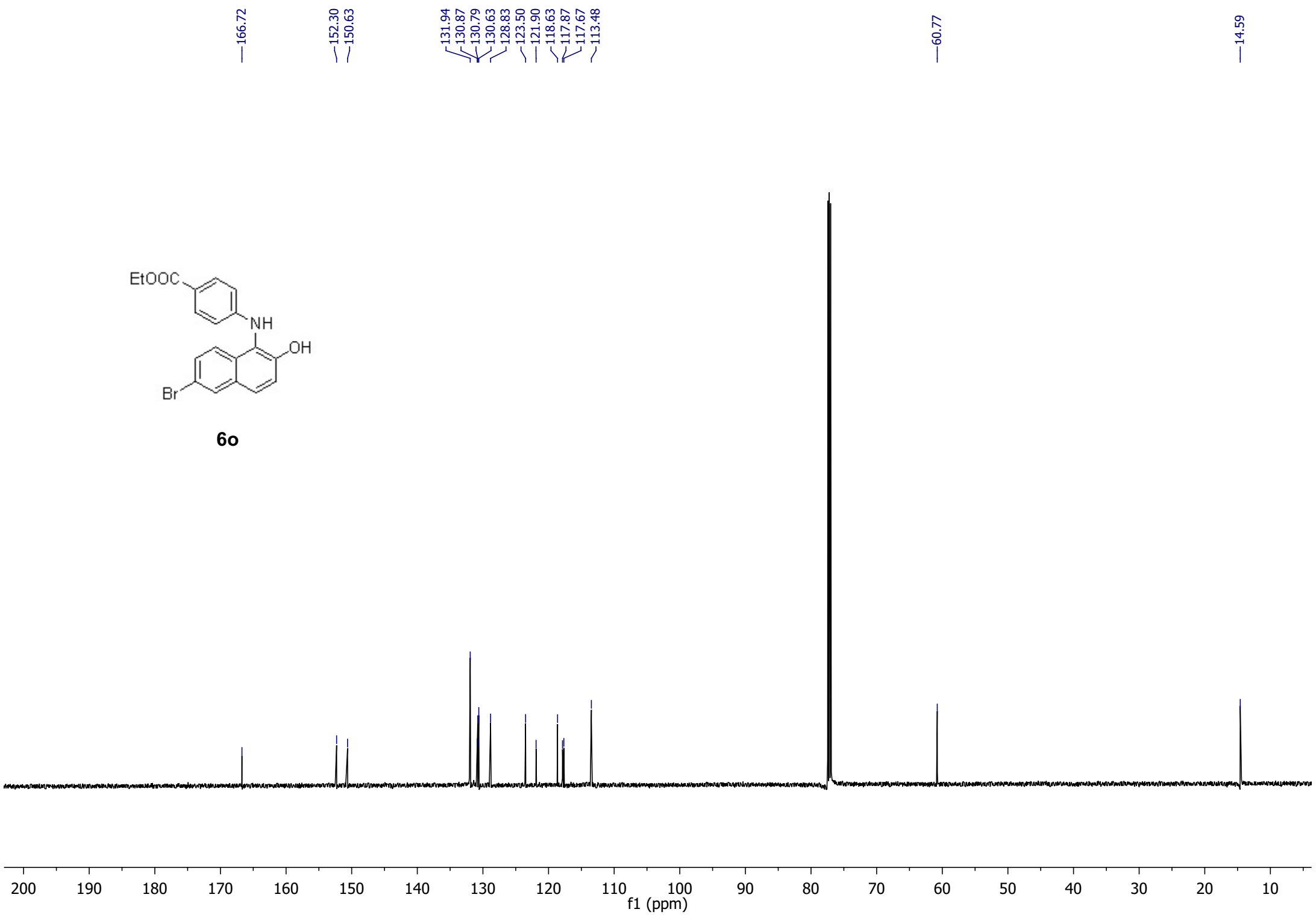

166.77
152.77
150.36
133.45
131.99
130.48
129.69
128.16
127.40
123.84
122.16
121.95
117.91
116.91
113.39
60.76
14.60
EtOOC
NH
Br
OH
6m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.850
7.836
7.717
7.709
7.702
7.694
7.151
7.137
6.993
6.974
6.838
6.602
6.589
5.576
4.311
4.299
4.287
4.275
3.685
1.348
1.336
1.324
EtOOC
NH
O
OH
6n
2.18
1.00
1.15
1.00
1.24
1.06
2.03
0.97
2.34
3.22
3.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

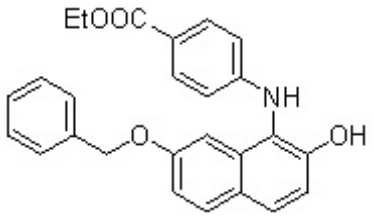

166.85
159.05
152.57
150.89
133.45
131.87
130.48
129.43
124.99
121.53
116.93
115.94
114.60
113.45
100.72
60.71
55.35
14.59
EtOOC
NH
O
OH
6n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.974
7.869
7.854
7.714
7.699
7.494
7.479
7.449
7.446
7.434
7.431
7.337
7.322
6.598
6.584
6.415
5.610
4.320
4.309
4.297
4.285
1.351
1.339
1.328
EtOOC
NH
OH
Br
1.00
1.92
1.01
1.01
0.93
0.97
1.91
0.82
0.95
2.13
3.02
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

6o

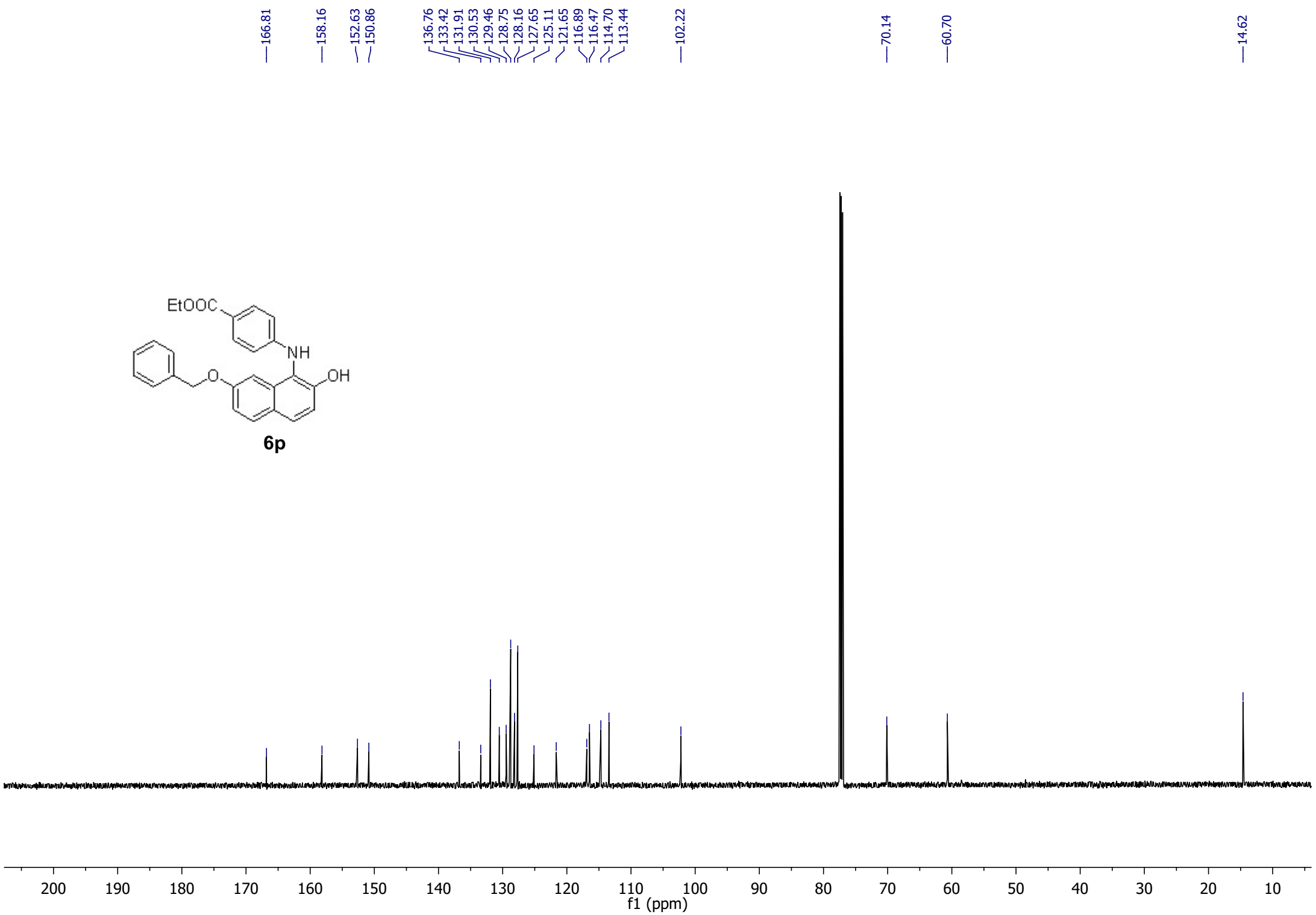

166.72
152.30
150.63
131.94
130.87
130.79
130.63
128.83
123.50
121.90
118.63
117.87
117.67
113.48
60.77
14.59
EtOOC
NH
OH
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

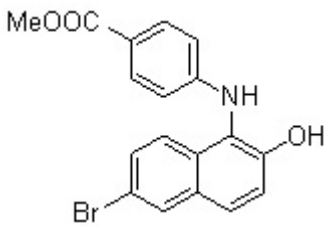
6o


EtOOC
NH
O
OH

6p

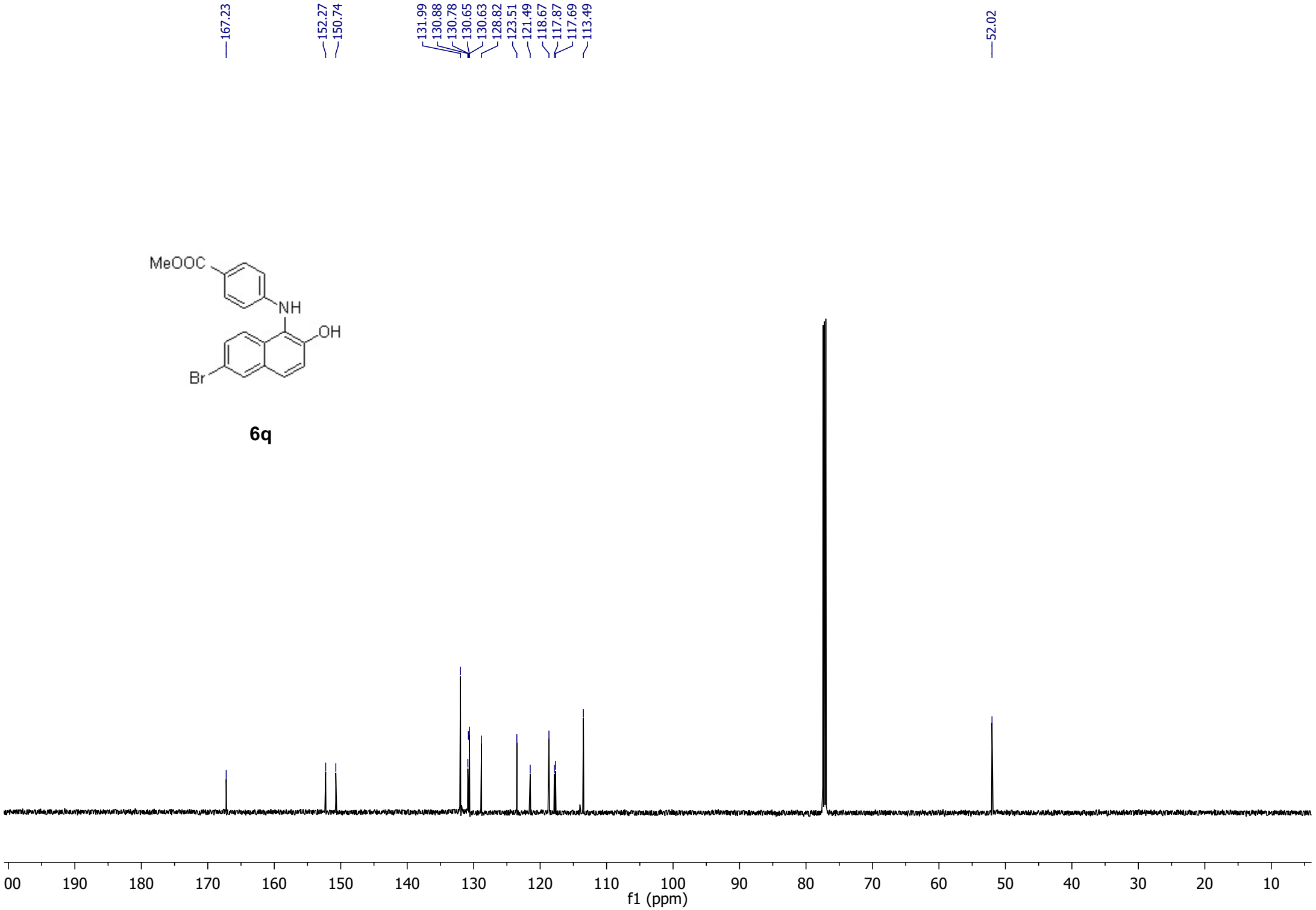
7.860
7.845
7.725
7.710
7.693
7.297
7.290
7.277
7.270
7.264
7.146
7.131
7.069
7.065
7.054
7.050
6.917
6.589
6.575
5.464
4.953
4.336
4.324
4.312
4.300
1.366
1.354
1.343
2.17
2.28
3.97
0.95
1.06
1.08
1.00
1.98
0.92
2.05
2.32
3.42
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

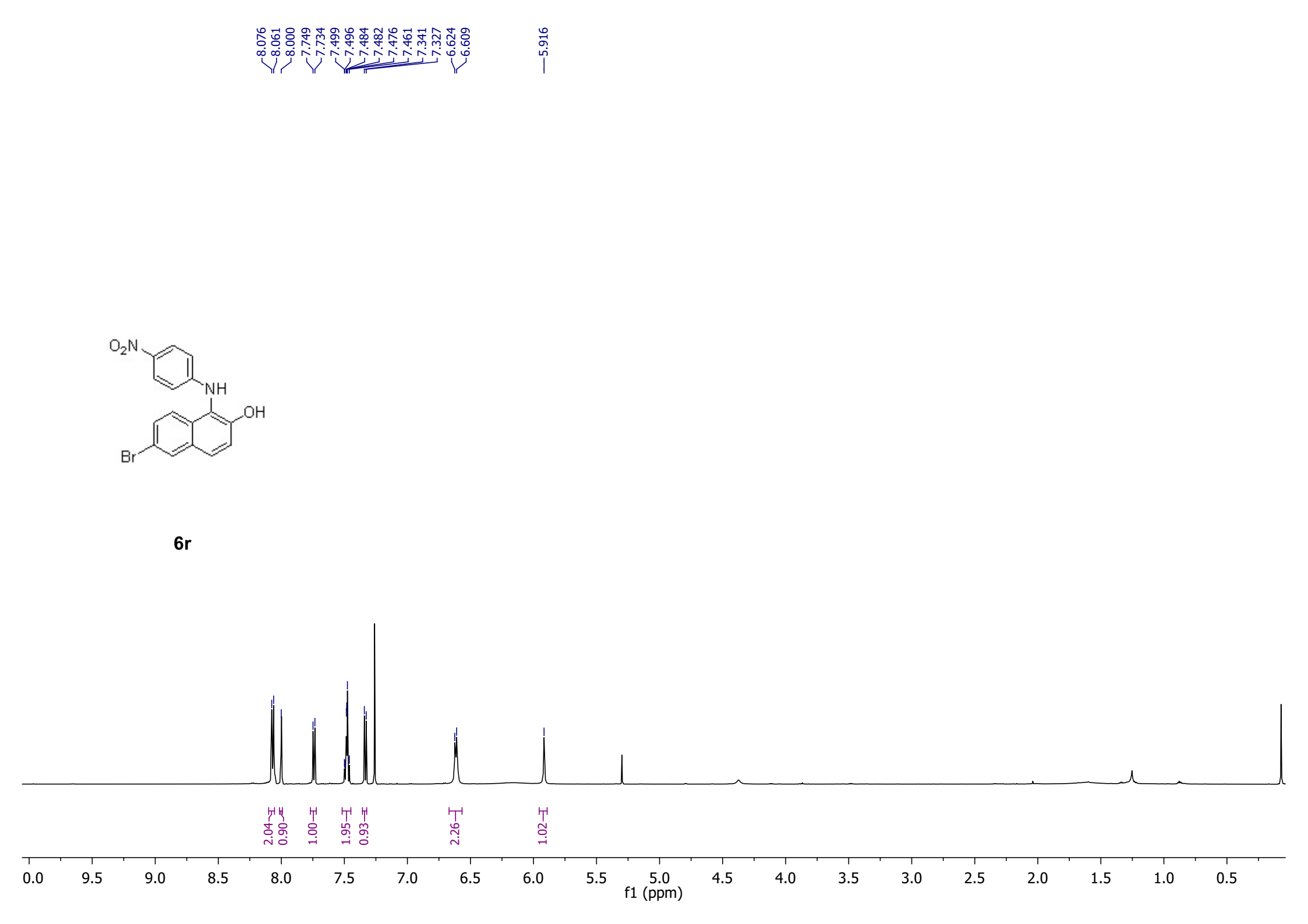

166.81
158.16
152.63
150.86
136.76
133.42
131.91
130.53
129.46
128.75
128.16
127.65
125.11
121.65
116.89
116.47
114.70
113.44
102.22
70.14
60.70
14.62
EtOOC
NH
O
OH
6p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


MeOOC
NH
OH
Br

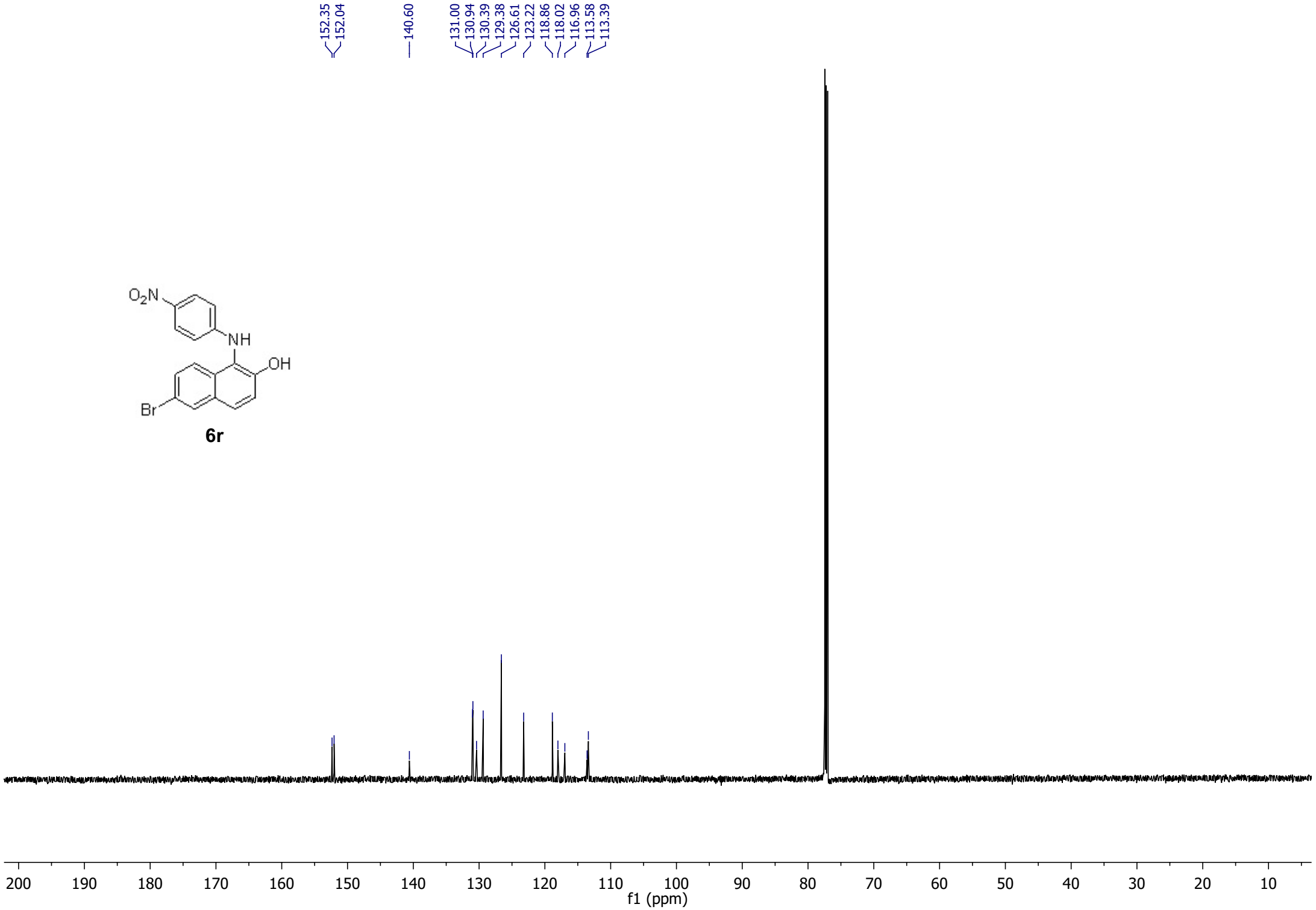
6q

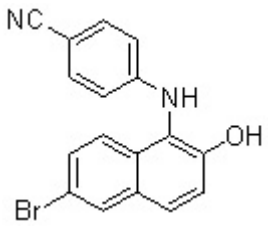
7.973
7.851
7.836
7.707
7.692
7.494
7.479
7.448
7.430
7.333
7.318
6.590
6.576
6.434
5.629
3.839
1.00
2.07
1.00
1.04
1.00
1.00
1.85
0.71
0.98
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


167.23
152.27
150.74
131.99
130.88
130.78
130.65
130.63
128.82
123.51
121.49
118.67
117.87
117.69
113.49
52.02
MeOOC
NH
OH
Br
6q
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.076
8.061
8.000
7.749
7.734
7.499
7.496
7.484
7.482
7.476
7.461
7.341
7.327
6.624
6.609
5.916
O2N
NH
OH
Br
2.04
0.90
1.00
1.95
0.93
2.26
1.02
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

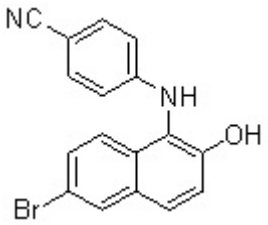
6r


152.35
152.04
140.60
131.00
130.94
130.39
129.38
126.61
123.22
118.86
118.02
116.96
113.58
113.39
O2N
NH
OH
Br
6r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


NC
NH
OH
Br

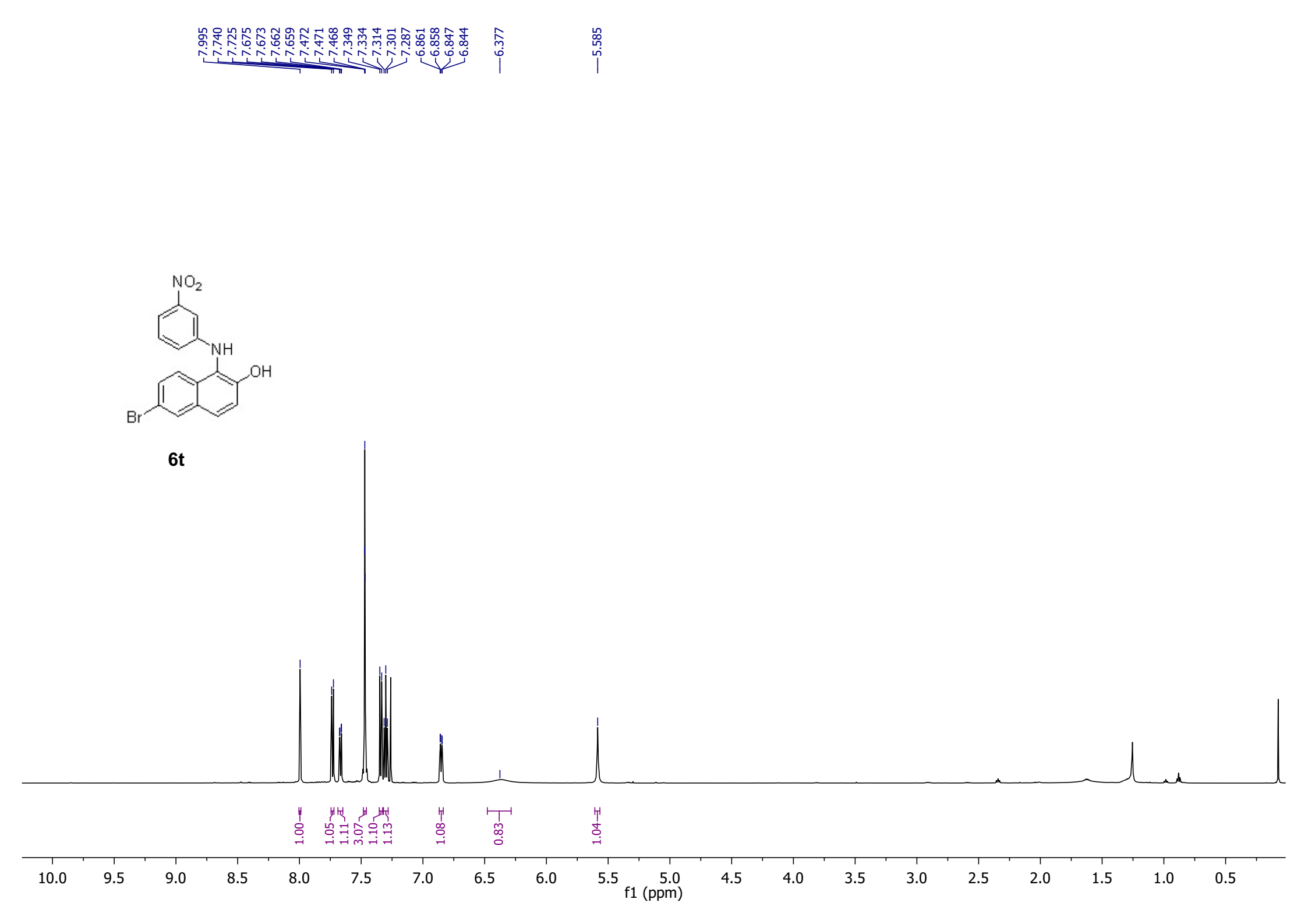
6s

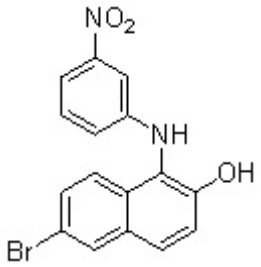
7.985
7.727
7.712
7.472
7.469
7.434
7.419
7.330
7.315
6.628
6.614
5.731
0.93
1.00
1.84
1.91
0.99
1.98
0.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


NC
NH
OH
Br

6s

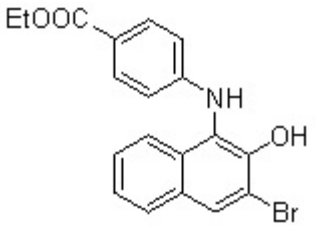
152.18
150.36
134.29
130.90
130.87
130.44
129.18
123.28
119.83
118.74
117.87
117.11
114.28
102.35
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.995
7.740
7.725
7.675
7.673
7.662
7.659
7.472
7.471
7.468
7.349
7.334
7.314
7.301
7.287
6.861
6.858
6.847
6.844
6.377
5.585
NO2
NH
OH
Br
6t
1.00
1.05
1.11
3.07
1.10
1.13
1.08
0.83
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


NO2
NH
OH
Br

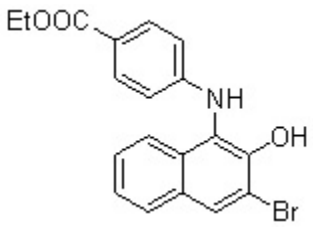
6t

152.41
149.70
147.78
131.00
130.86
130.64
130.43
129.20
123.17
119.91
118.66
117.82
117.58
114.91
108.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


EtOOC
NH
OH
Br

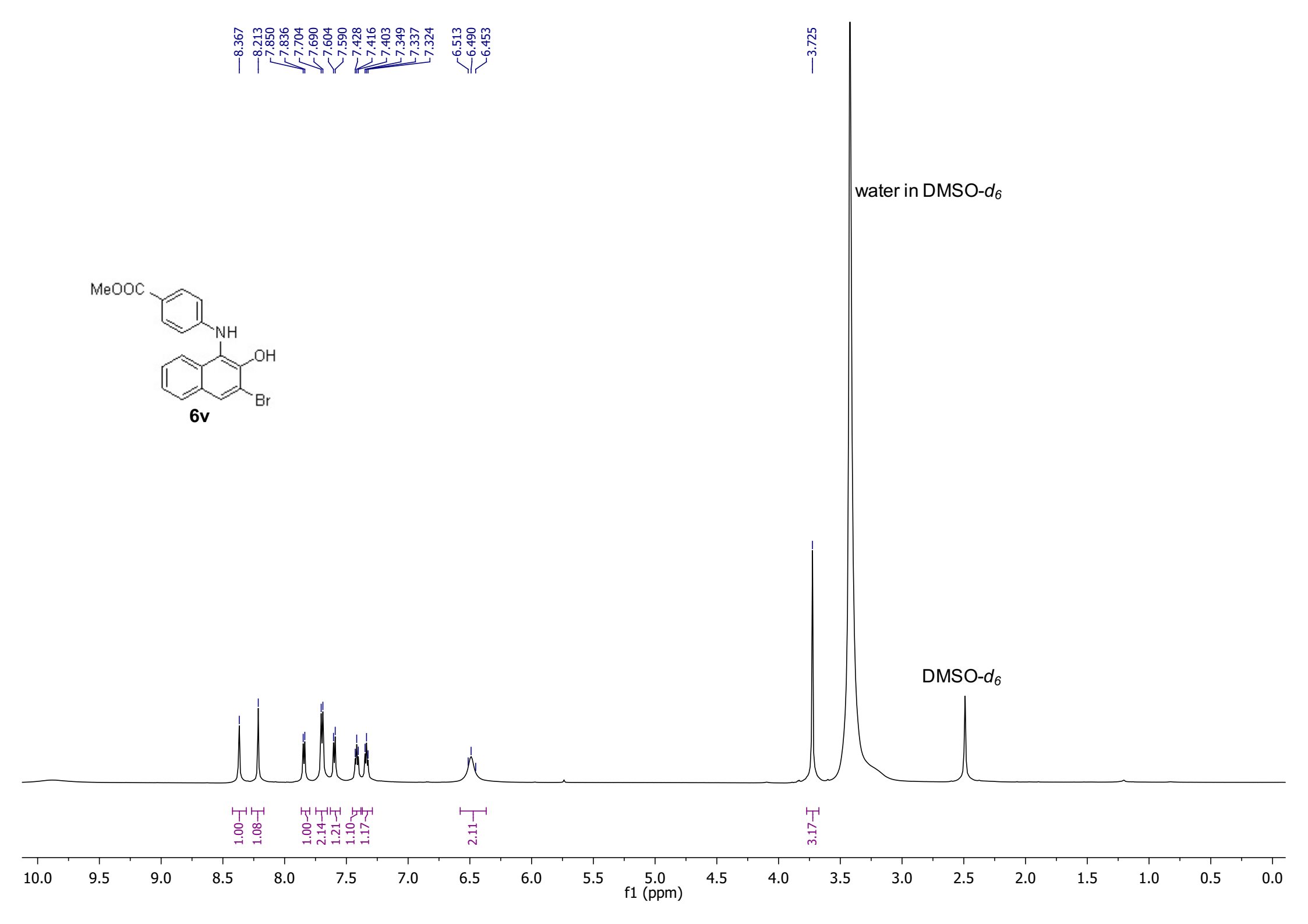
6u

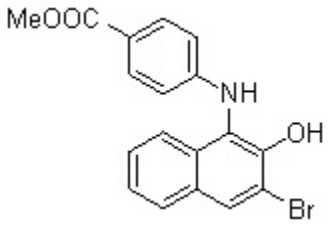
8.066
7.880
7.858
7.758
7.738
7.650
7.627
7.429
7.415
7.395
7.368
7.351
6.627
6.605
6.402
5.806
4.335
4.317
4.299
4.281
1.359
1.341
1.323
1.00
2.00
0.98
0.98
2.02
2.16
0.85
0.93
2.21
3.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


EtOOC
NH
OH
Br

6u

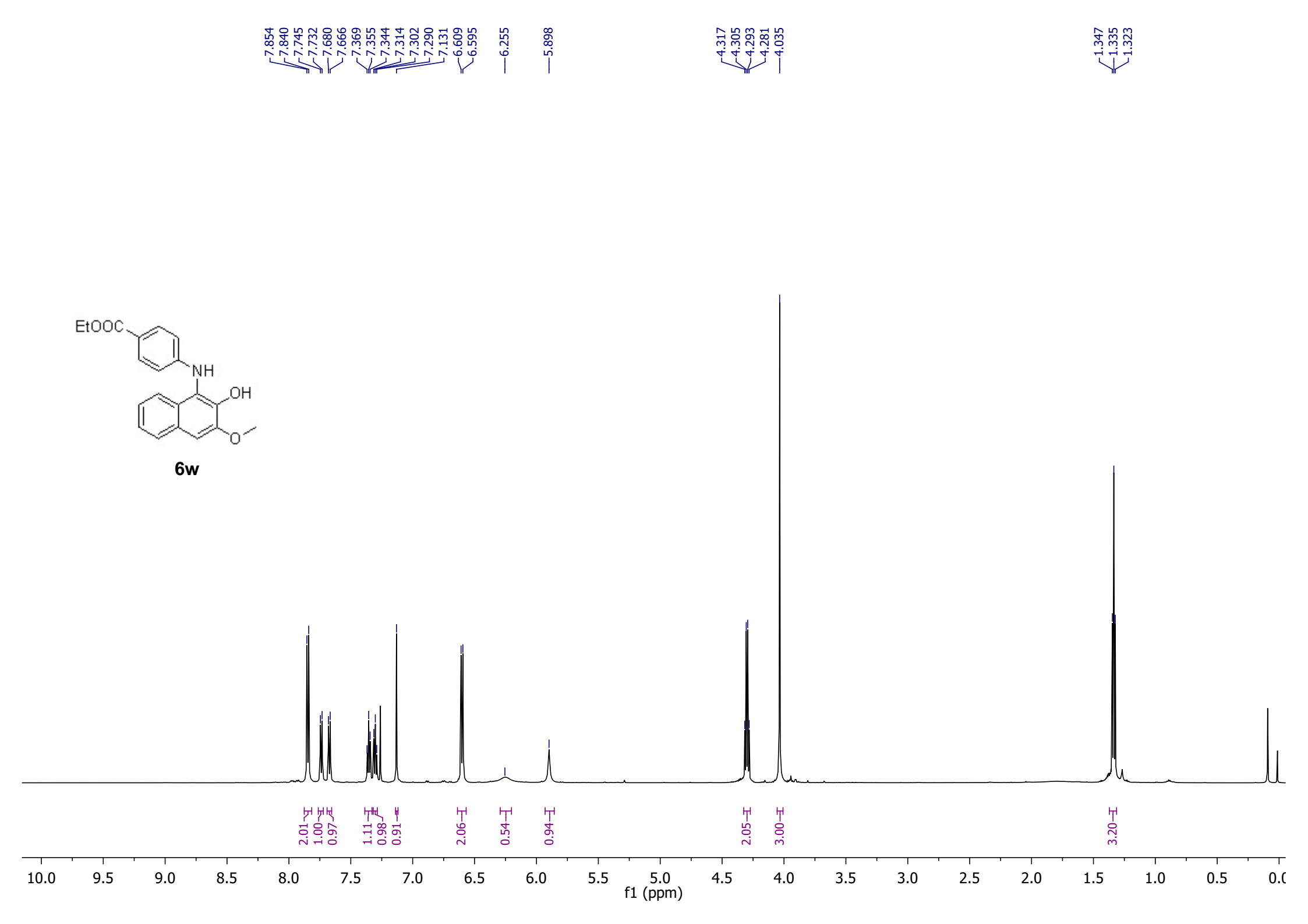
166.68
150.46
147.89
131.79
131.21
131.06
129.81
127.87
127.62
125.03
122.37
122.07
119.78
113.89
111.40
60.69
14.62
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

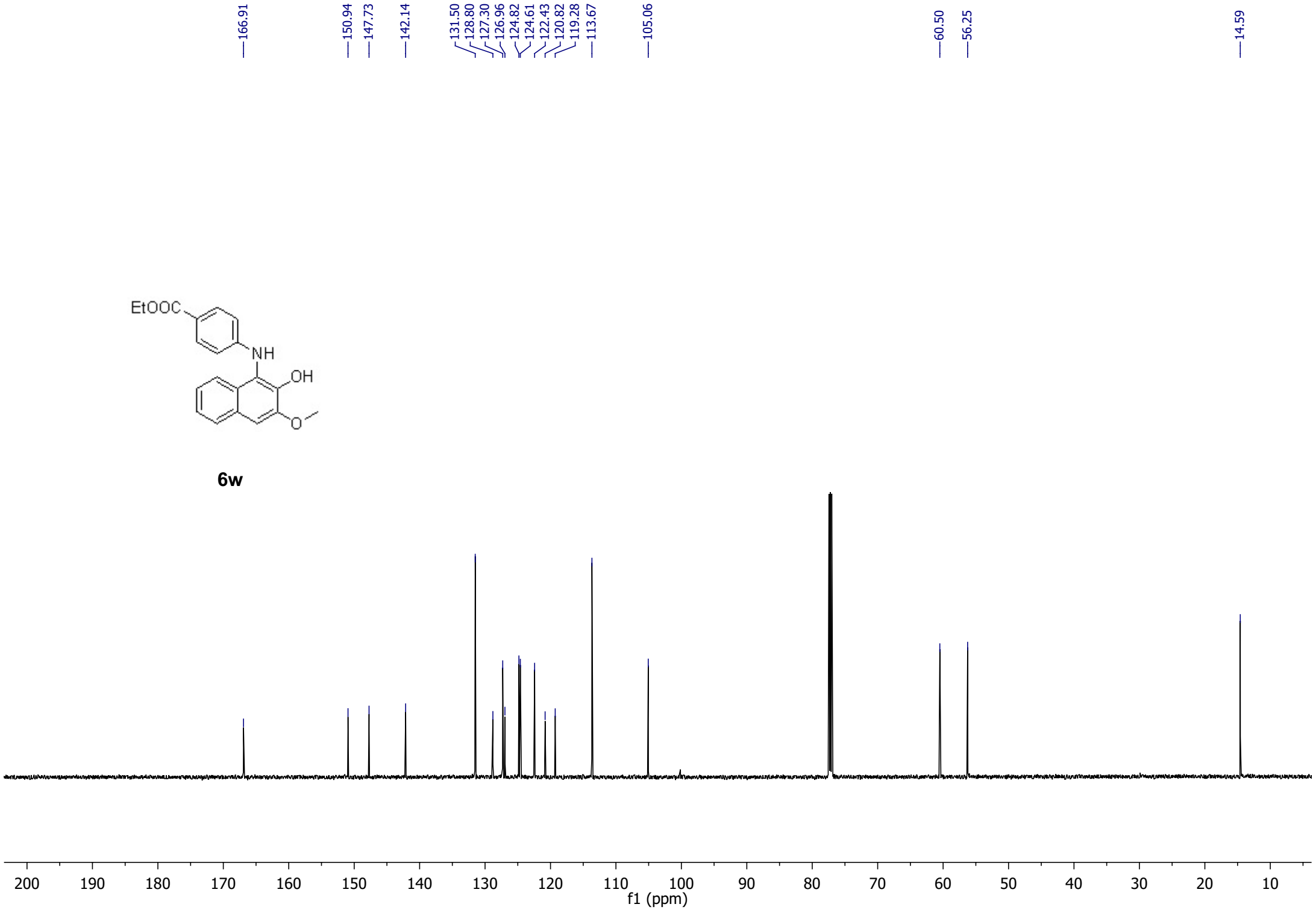

8.367
8.213
7.850
7.836
7.704
7.690
7.604
7.590
7.428
7.416
7.403
7.349
7.337
7.324
6.513
6.490
6.453
3.725
water in DMSO-d_6
DMSO-d_6
MeOOC
NH
OH
Br
6v
1.00
1.08
1.00
2.14
1.21
1.10
1.17
2.11
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

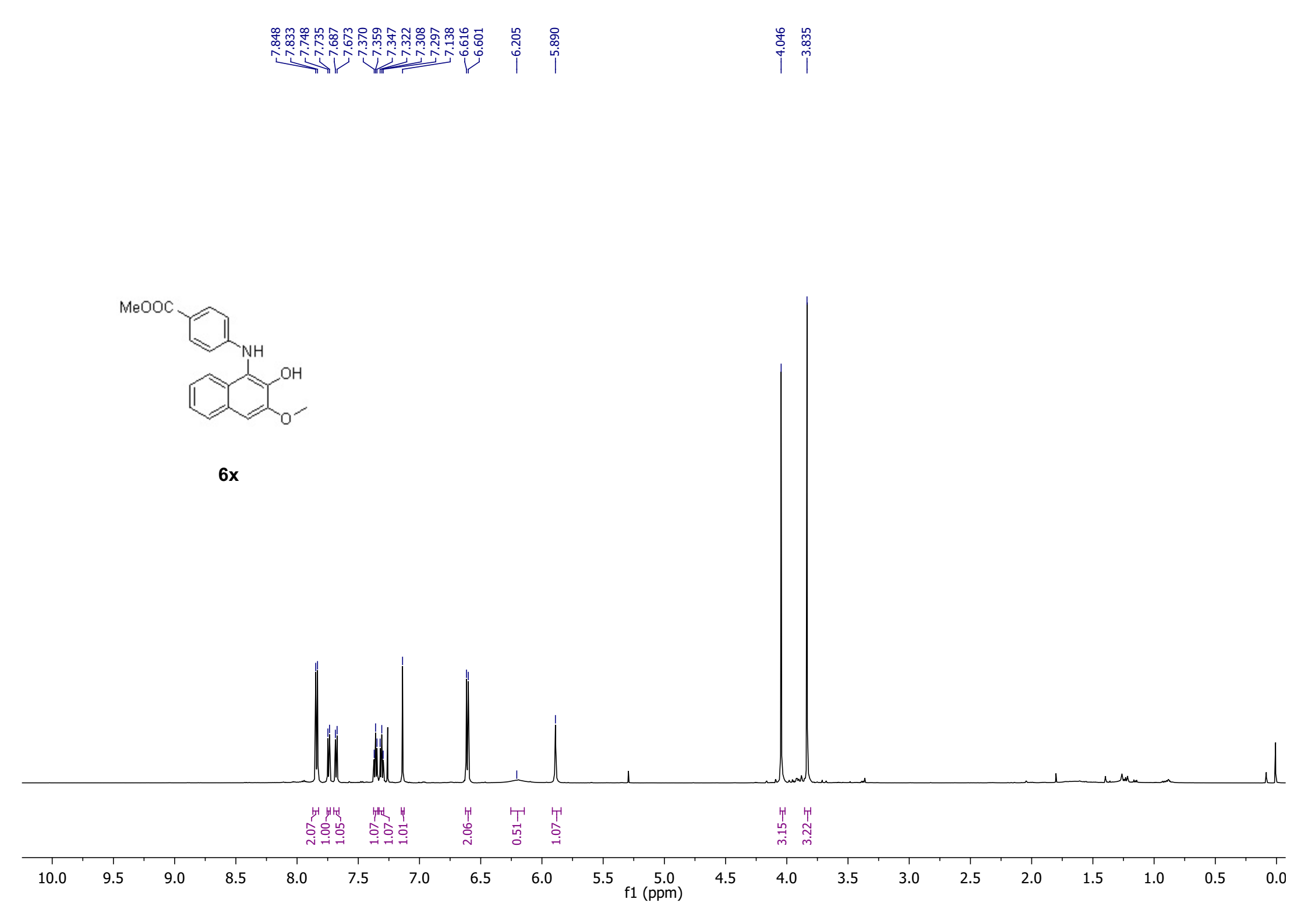

MeOOC
NH
OH
Br

6v

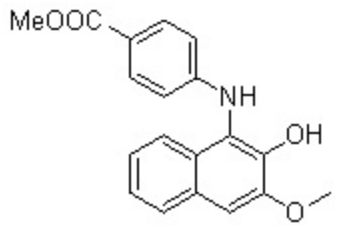
166.36
152.04
148.86
131.22
130.98
130.54
128.93
127.54
126.96
124.24
122.28
120.13
117.76
113.15
112.75
51.48
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


7.854
7.840
7.745
7.732
7.680
7.666
7.369
7.355
7.344
7.314
7.302
7.290
7.131
6.609
6.595
6.255
5.898
4.317
4.305
4.293
4.281
4.035
1.347
1.335
1.323
EtOOC
NH
OH
O
6w
2.01
1.00
0.97
1.11
0.98
0.91
2.06
0.54
0.94
2.05
3.00
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.91
150.94
147.73
142.14
131.50
128.80
127.30
126.96
124.82
124.61
122.43
120.82
119.28
113.67
105.06
60.50
56.25
14.59
EtOOC
NH
OH
O
6w
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

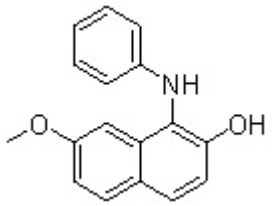

7.848
7.833
7.748
7.735
7.687
7.673
7.370
7.359
7.347
7.322
7.308
7.297
7.138
6.616
6.601
6.205
5.890
4.046
3.835
MeOOC
NH
OH
O
2.07
1.00
1.05
1.07
1.07
1.01
2.06
0.51
1.07
3.15
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

6x


MeOOC
NH
OH
O

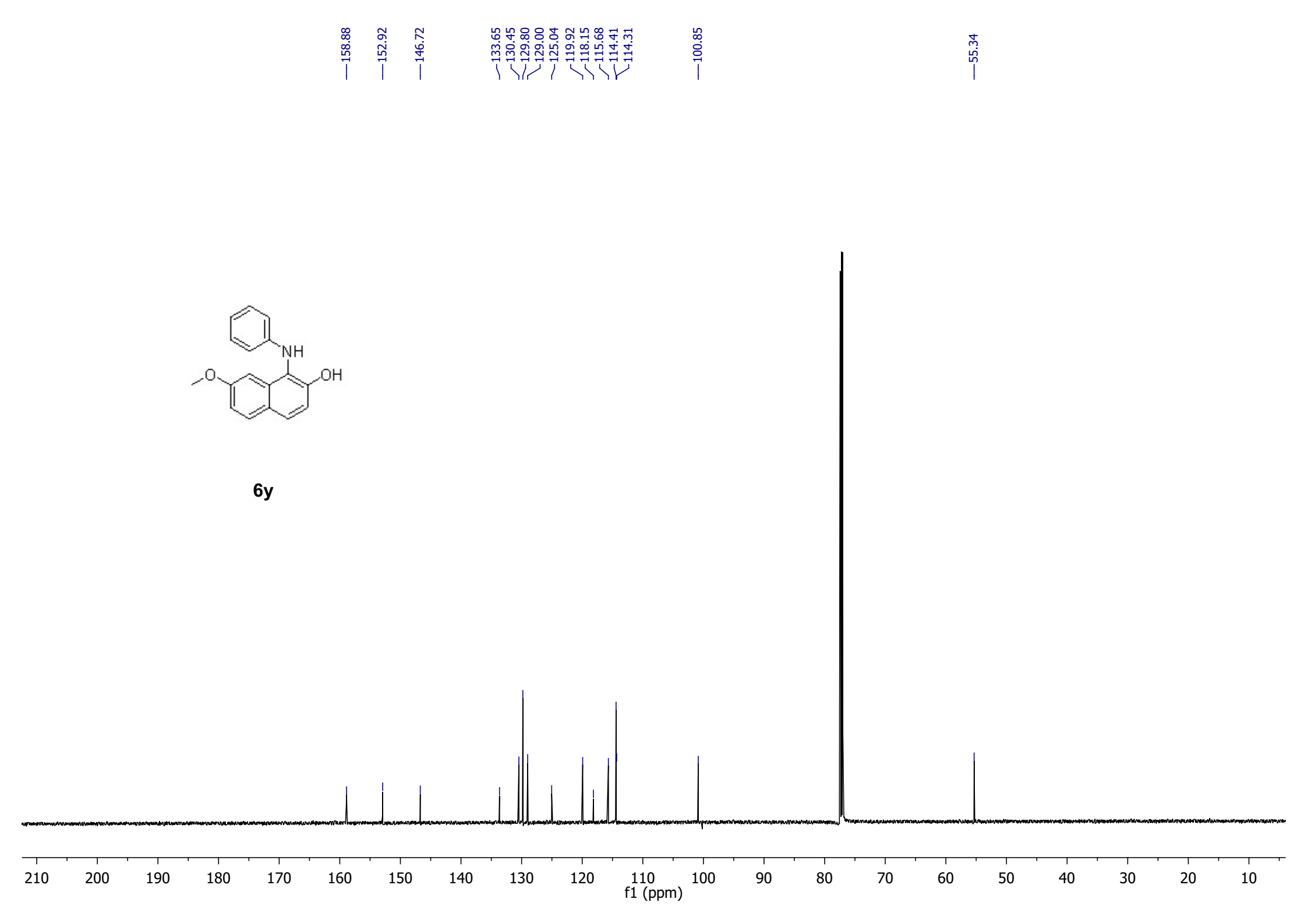
6x

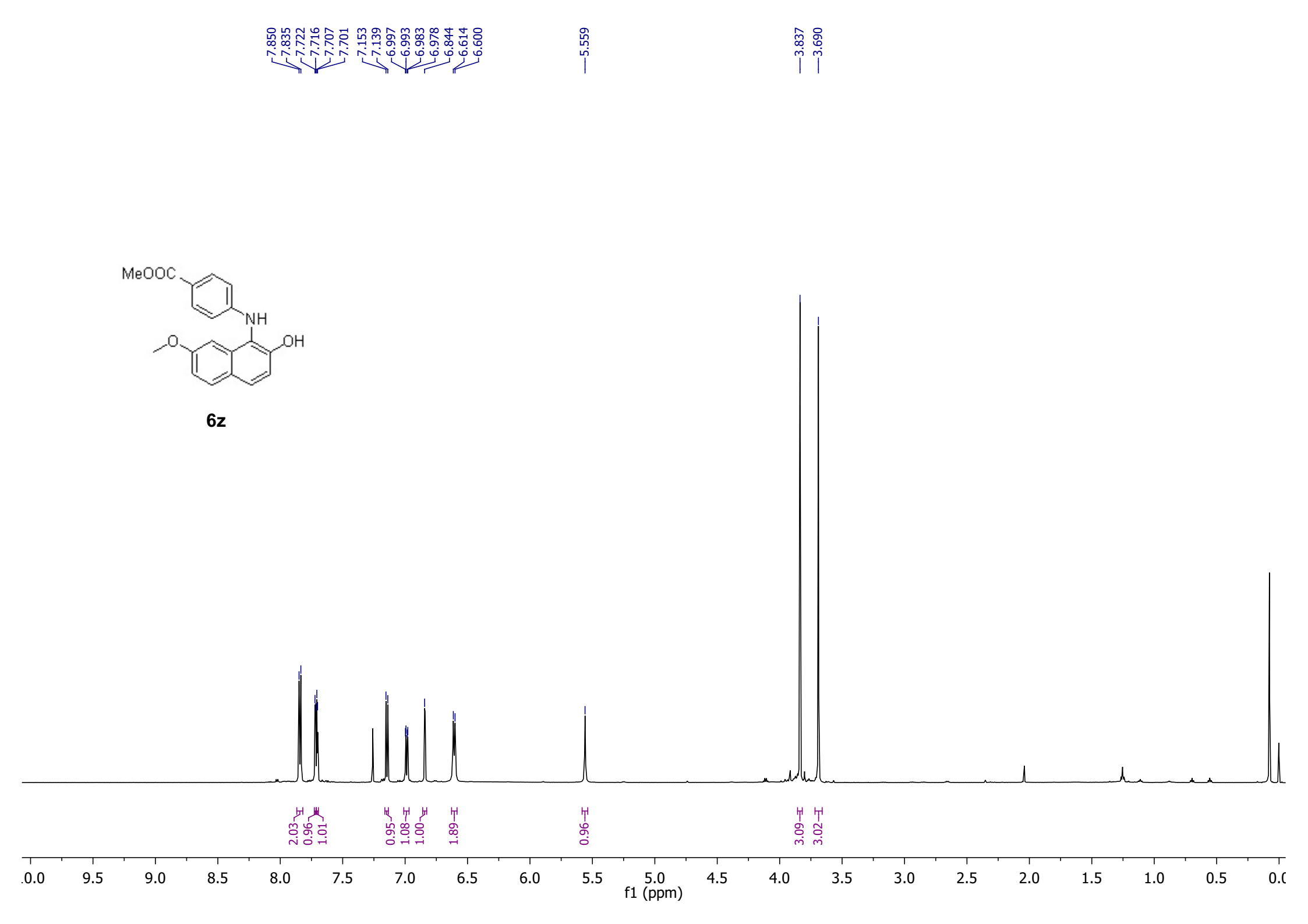
167.37
151.01
147.71
142.13
131.58
128.82
127.33
126.98
124.88
124.65
122.43
120.52
119.24
113.72
105.09
56.29
51.83
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

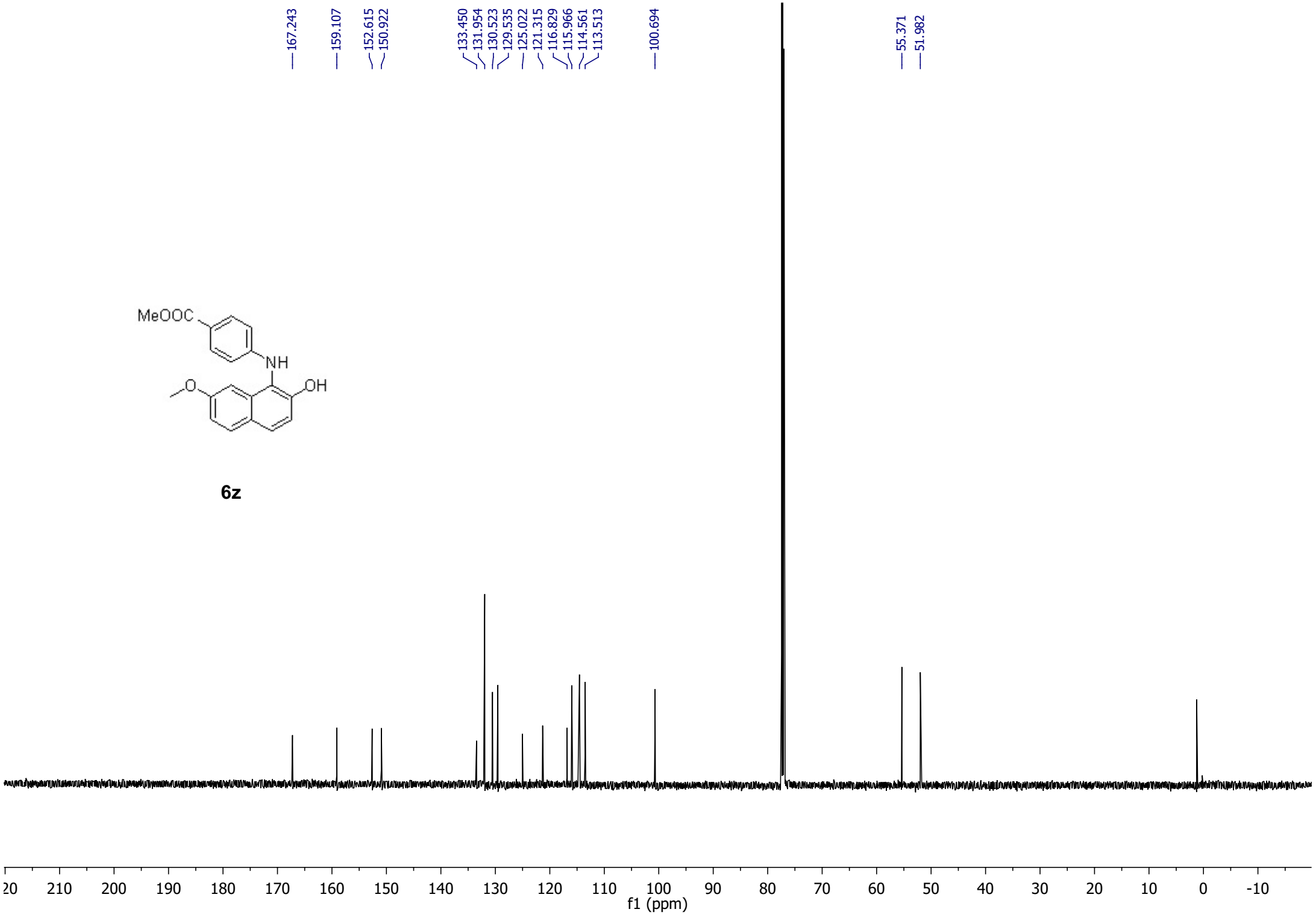

NH
O
OH

6y

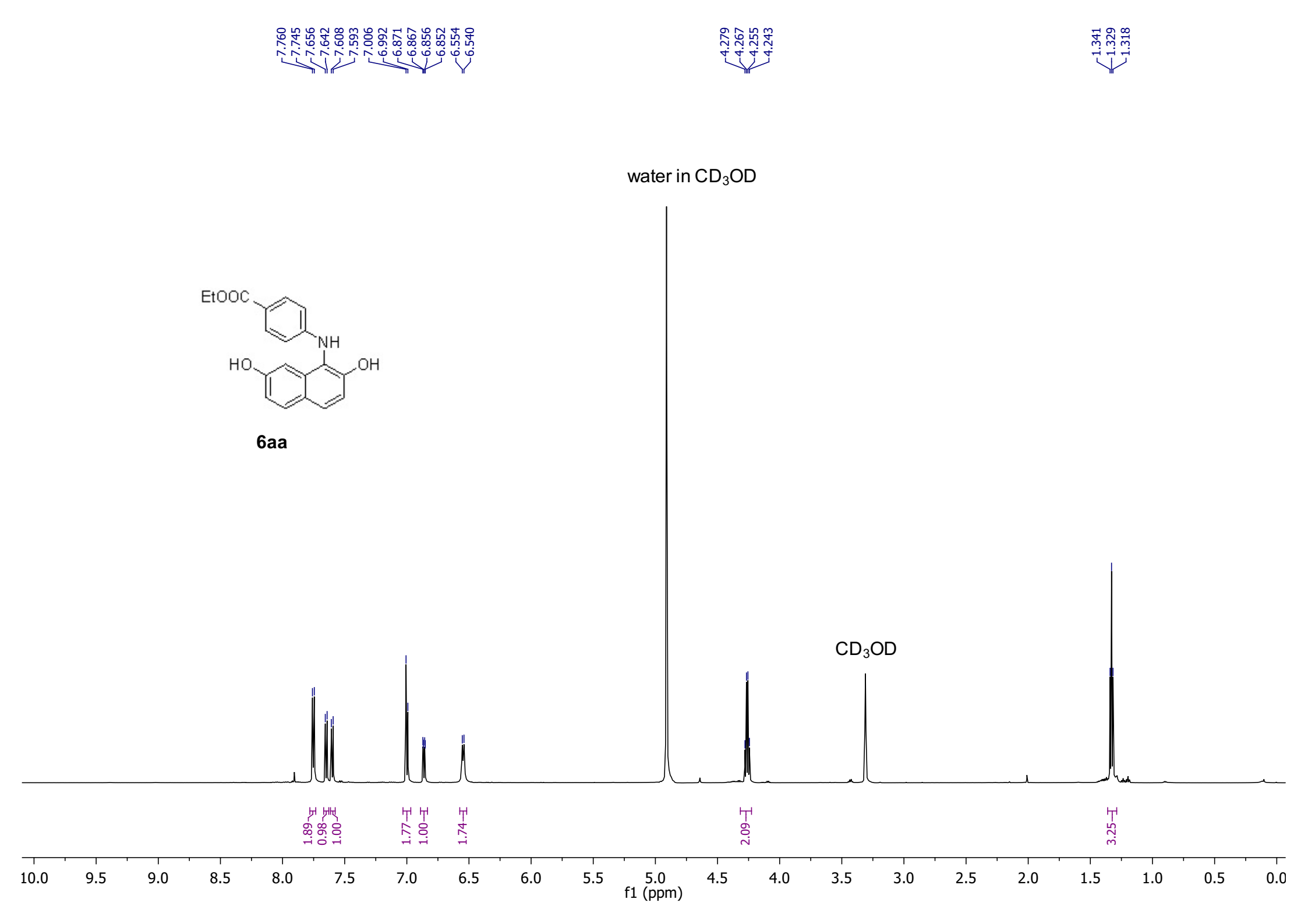
7.717
7.702
7.688
7.195
7.181
7.169
7.165
7.150
6.982
6.978
6.967
6.963
6.923
6.843
6.831
6.819
6.669
6.656
6.566
5.155
3.713
2.00
3.00
1.04
1.00
1.05
1.96
0.84
0.95
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

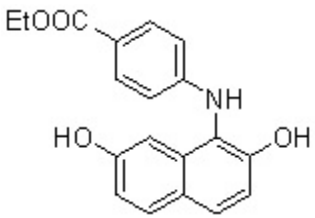

158.88
152.92
146.72
133.65
130.45
129.80
129.00
125.04
119.92
118.15
115.68
114.41
114.31
100.85
55.34
NH
O
OH
6y
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.850
7.835
7.722
7.716
7.707
7.701
7.153
7.139
6.997
6.993
6.983
6.978
6.844
6.614
6.600
5.559
3.837
3.690
MeOOC
NH
O
OH
6z
2.03
0.96
1.01
0.95
1.08
1.00
1.89
0.96
3.09
3.02
f1 (ppm)


167.243
159.107
152.615
150.922
133.450
131.954
130.523
129.535
125.022
121.315
116.829
115.966
114.561
113.513
100.694
55.371
51.982
MeOOC
NH
O
OH
f1 (ppm)

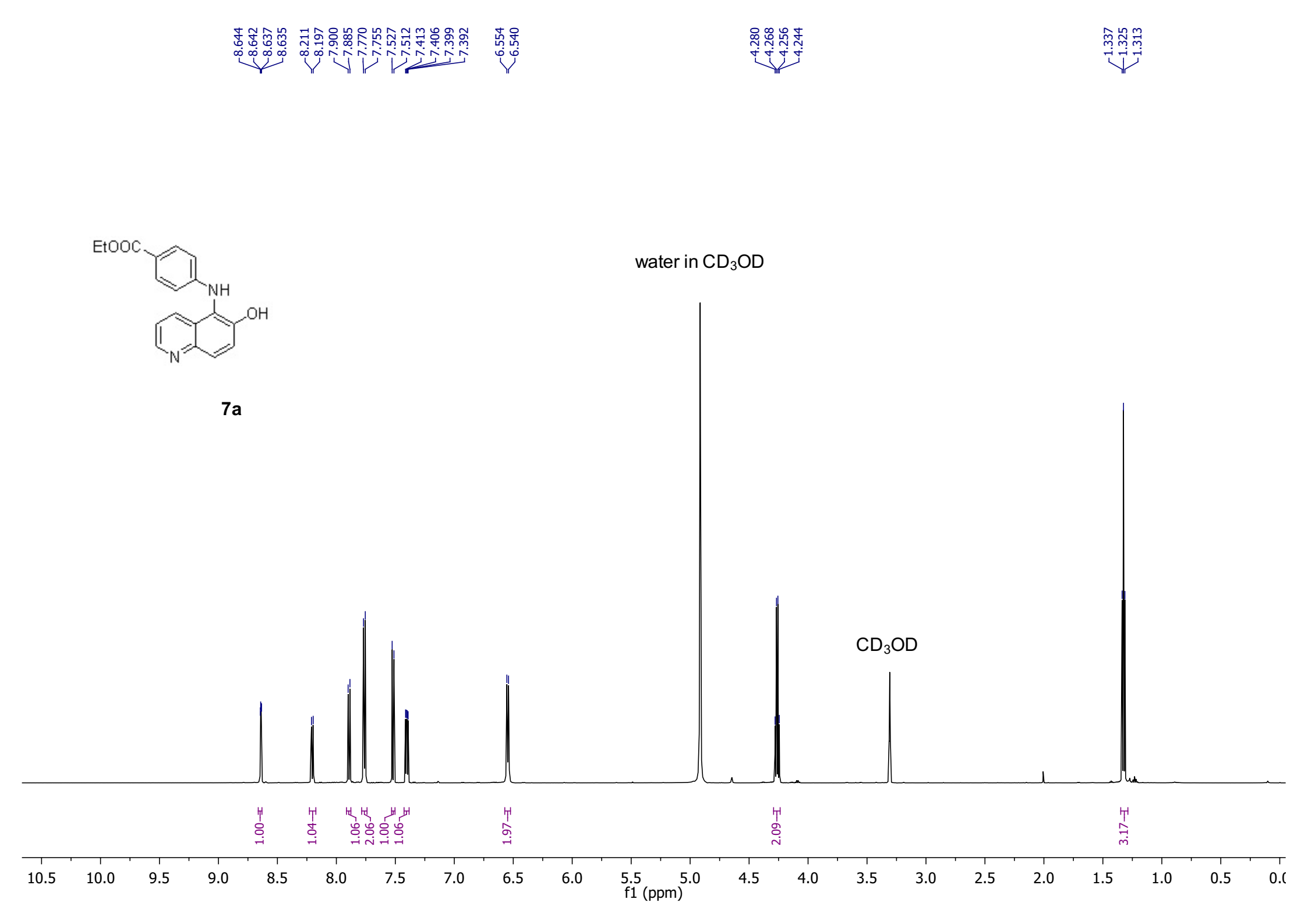
6z

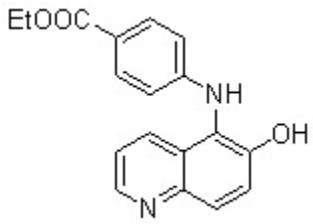

7.760
7.745
7.656
7.642
7.608
7.593
7.006
6.992
6.871
6.867
6.856
6.852
6.554
6.540
4.279
4.267
4.255
4.243
1.341
1.329
1.318
water in CD3OD
EtOOC
NH
HO
OH
6aa
CD3OD
1.89
0.98
1.00
1.77
1.00
1.74
2.09
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


EtOOC
NH
HO
OH

6aa

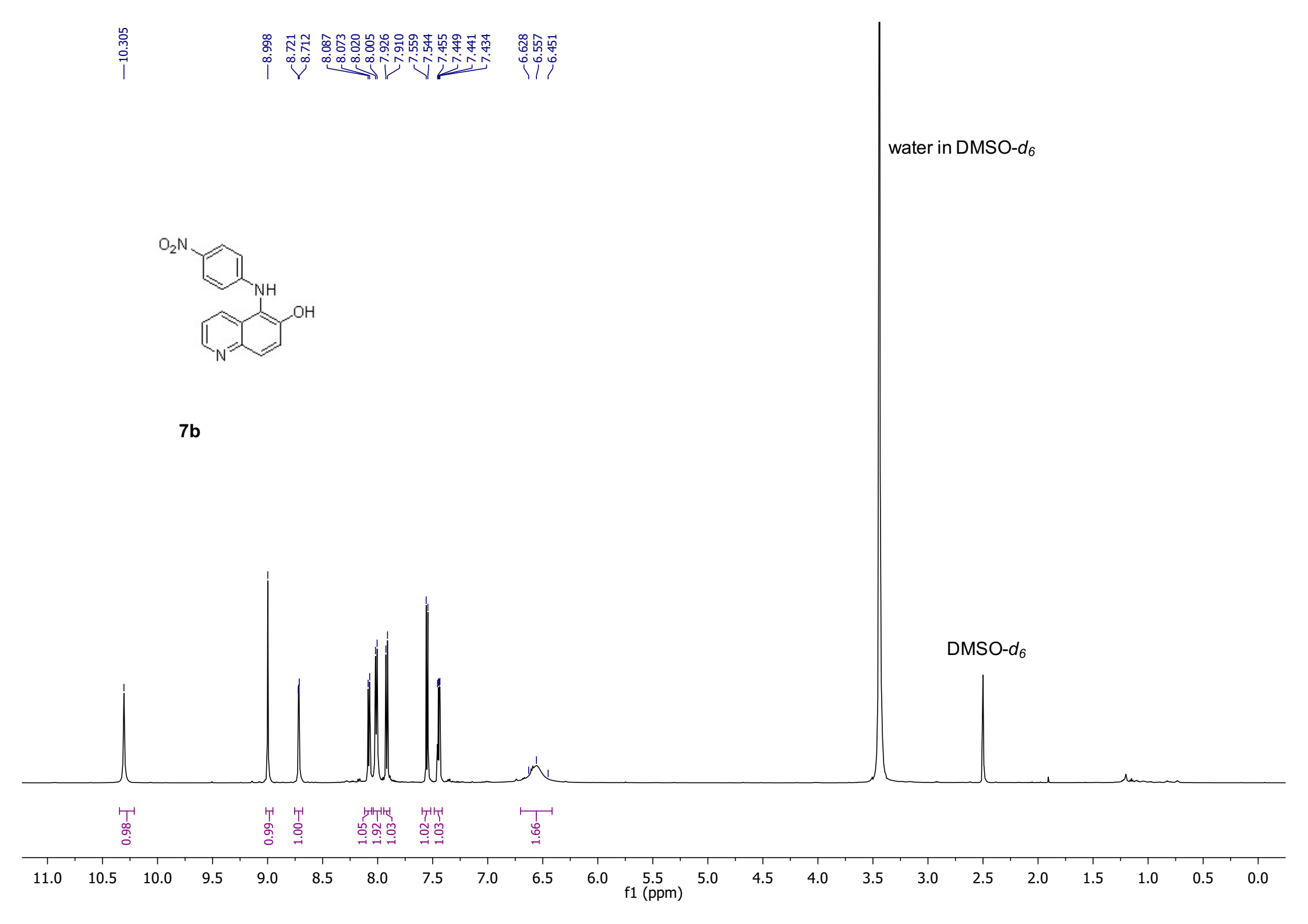
168.86
157.30
154.14
153.16
135.54
132.22
131.01
129.02
125.59
119.34
118.51
116.28
115.96
113.71
105.16
61.35
14.71
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.644
8.642
8.637
8.635
8.211
8.197
7.900
7.885
7.770
7.755
7.527
7.512
7.413
7.406
7.399
7.392
6.554
6.540
4.280
4.268
4.256
4.244
1.337
1.325
1.313
EtOOC
NH
OH
N
7a
water in CD3OD
CD3OD
1.00
1.04
1.06
2.06
1.00
1.06
1.97
2.09
3.17
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

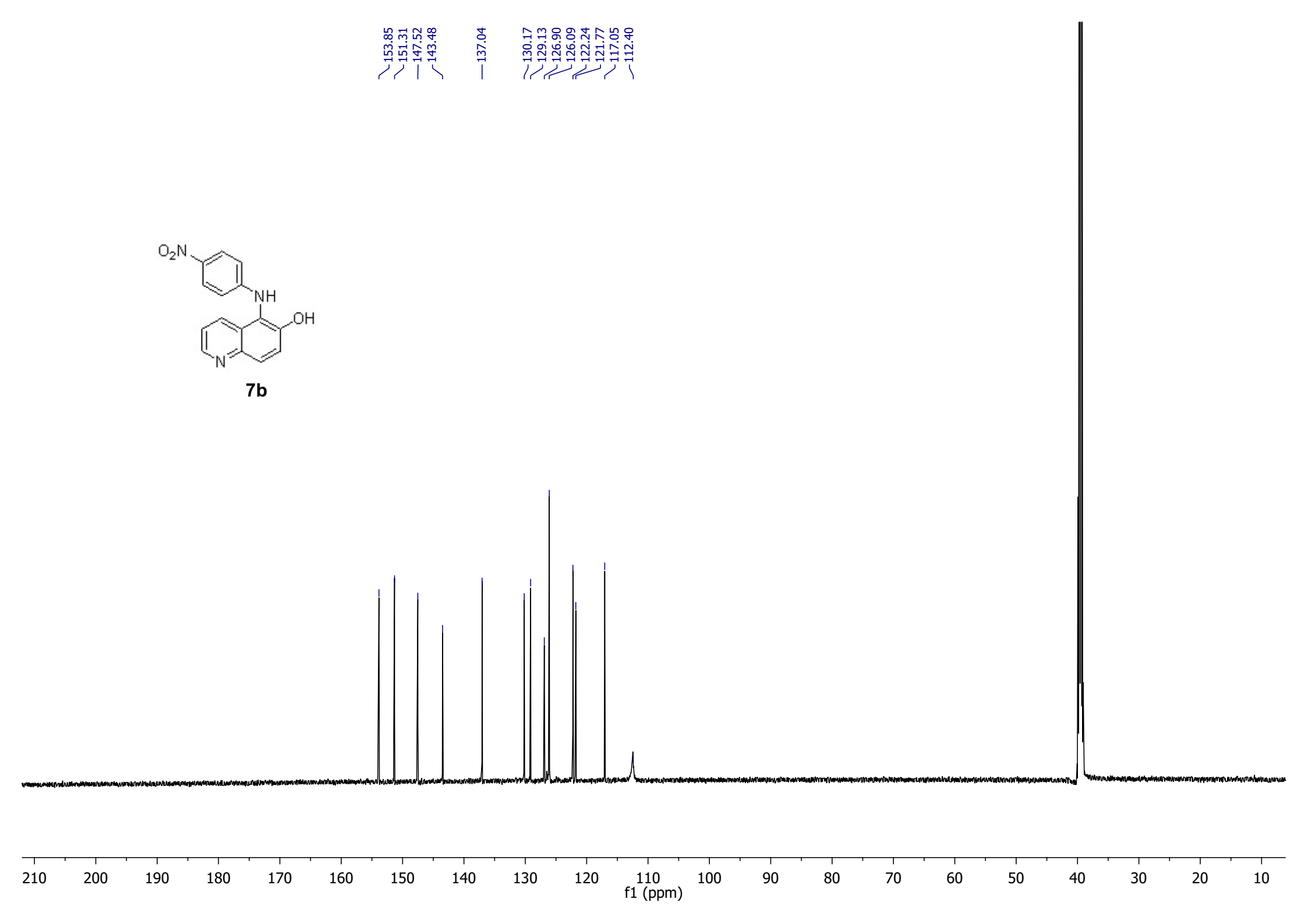

EtOOC
NH
OH
N

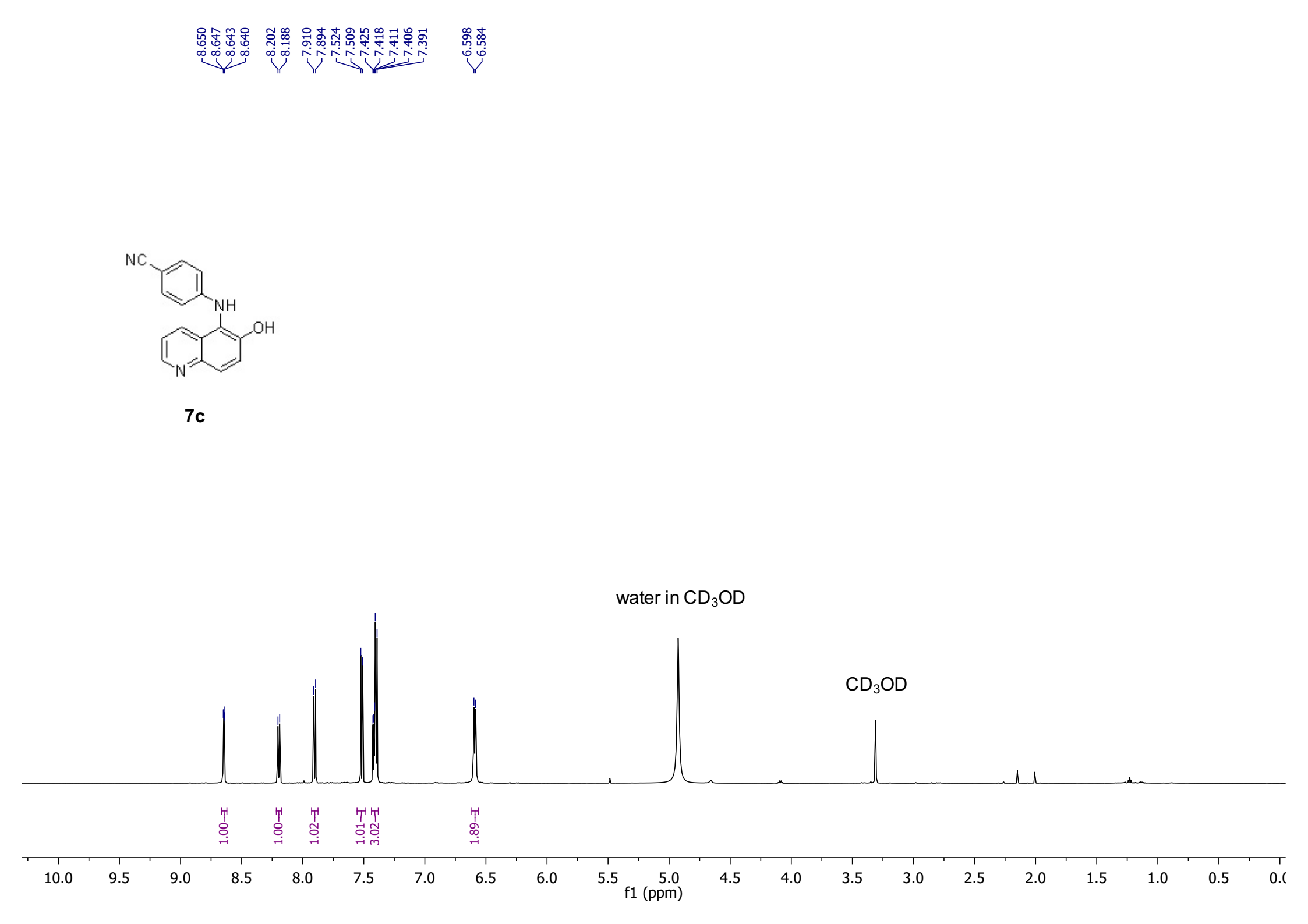
7a

168.63
153.52
153.38
148.04
144.56
132.98
132.27
129.13
128.81
123.60
122.51
120.09
119.92
113.84
61.43
14.70
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

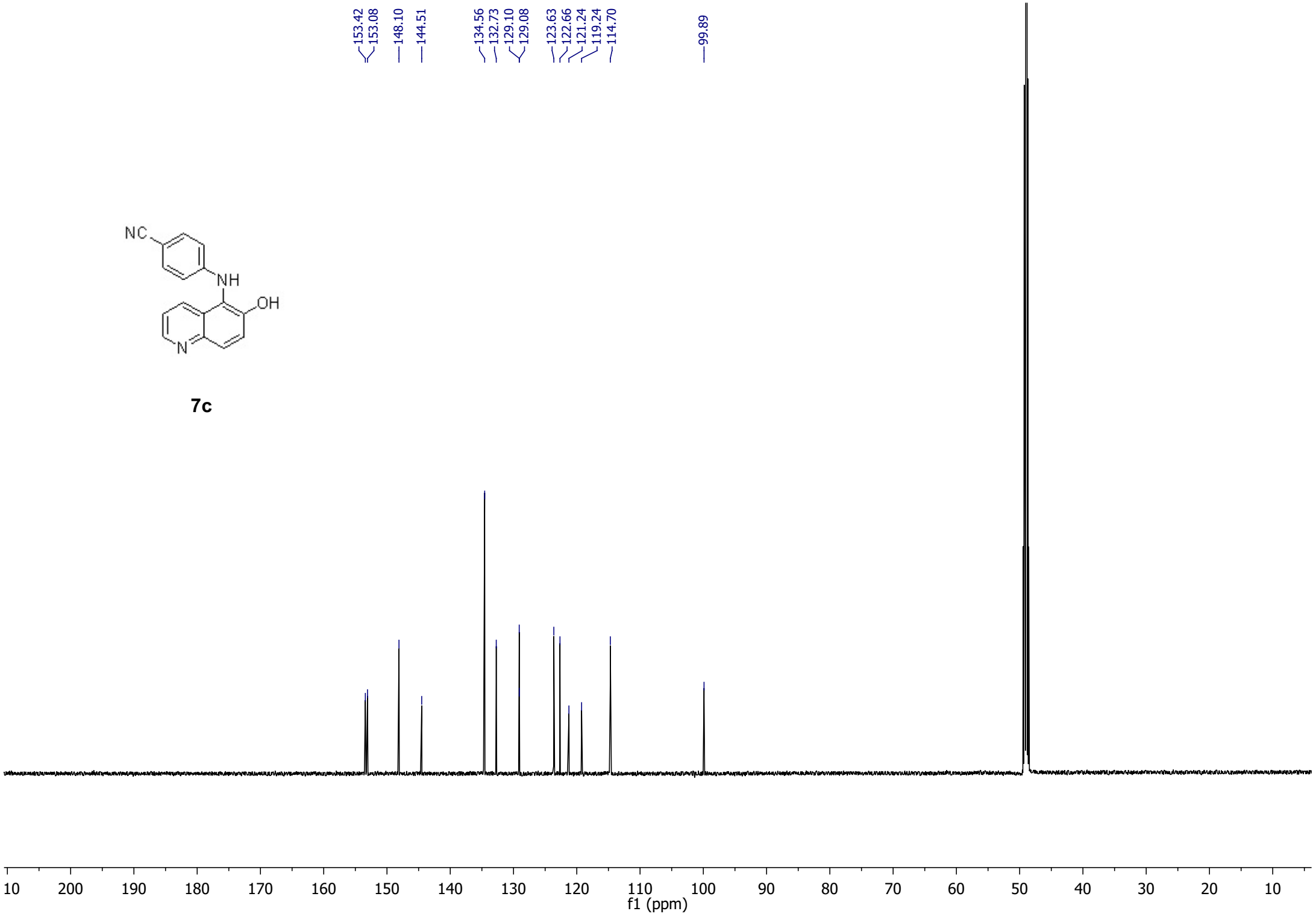

10.305
8.998
8.721
8.712
8.087
8.073
8.020
8.005
7.926
7.910
7.559
7.544
7.455
7.449
7.441
7.434
6.628
6.557
6.451
water in DMSO-d_6
DMSO-d_6
O_2N
NH
OH
N
0.98
0.99
1.00
1.05
1.92
1.03
1.02
1.03
1.66
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

7b

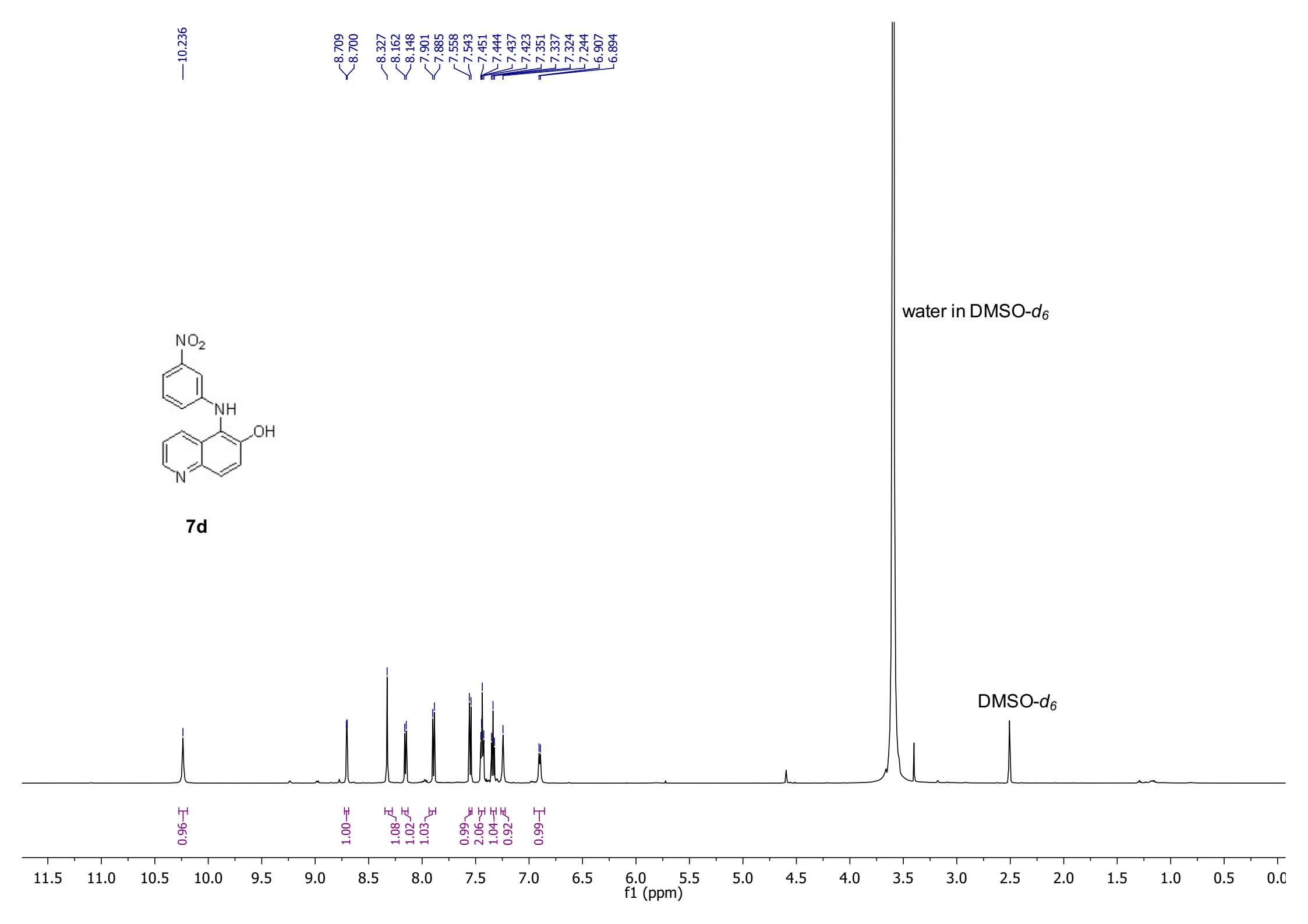

153.85
151.31
147.52
143.48
137.04
130.17
129.13
126.90
126.09
122.24
121.77
117.05
112.40
O2N
NH
OH
N
7b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.650
8.647
8.643
8.640
8.202
8.188
7.910
7.894
7.524
7.509
7.425
7.418
7.411
7.406
7.391
6.598
6.584
NC
NH
OH
N
water in CD3OD
CD3OD
1.00
1.00
1.02
1.01
3.02
1.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

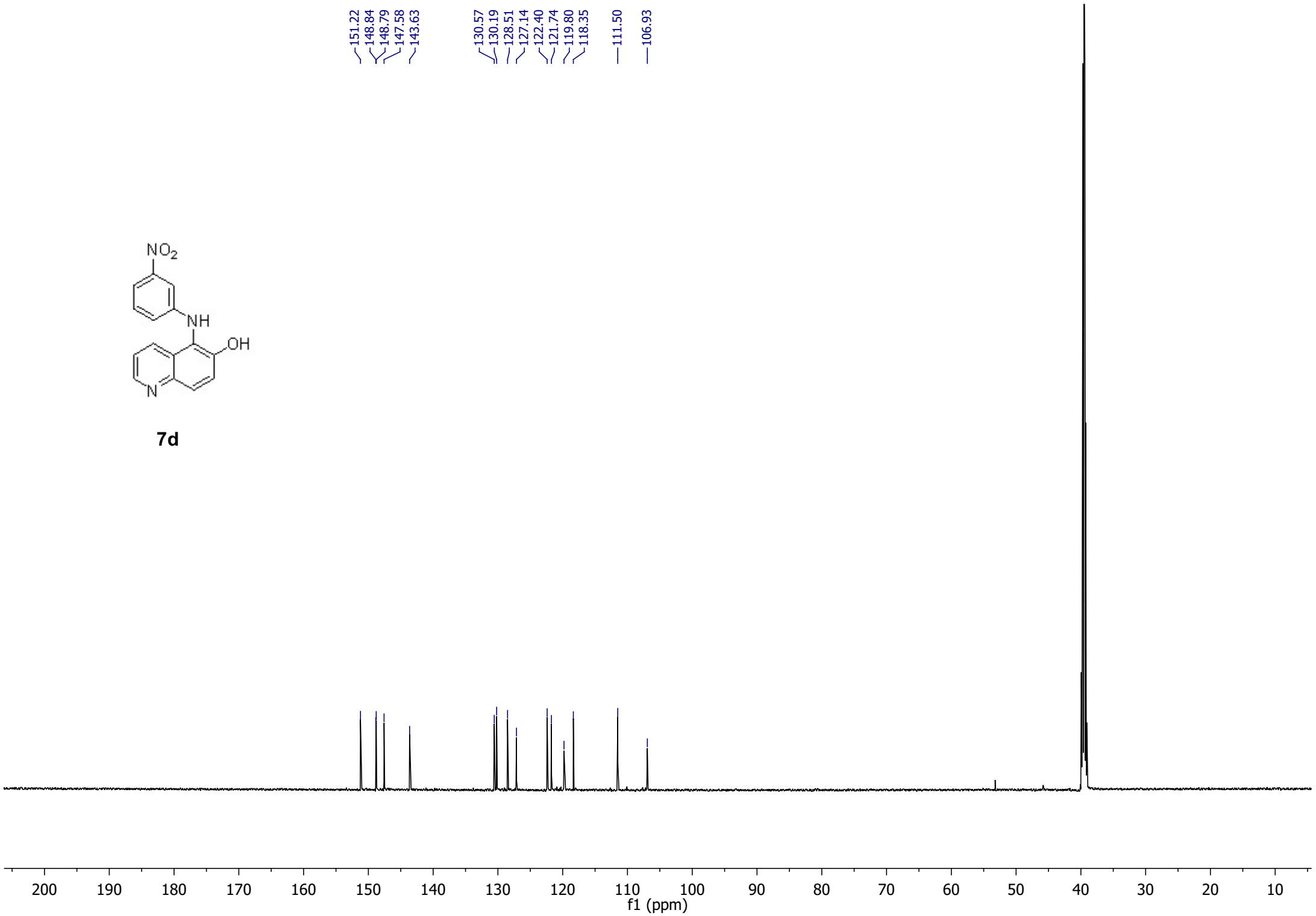
7c


153.42
153.08
148.10
144.51
134.56
132.73
129.10
129.08
123.63
122.66
121.24
119.24
114.70
99.89
NC
NH
OH
N
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

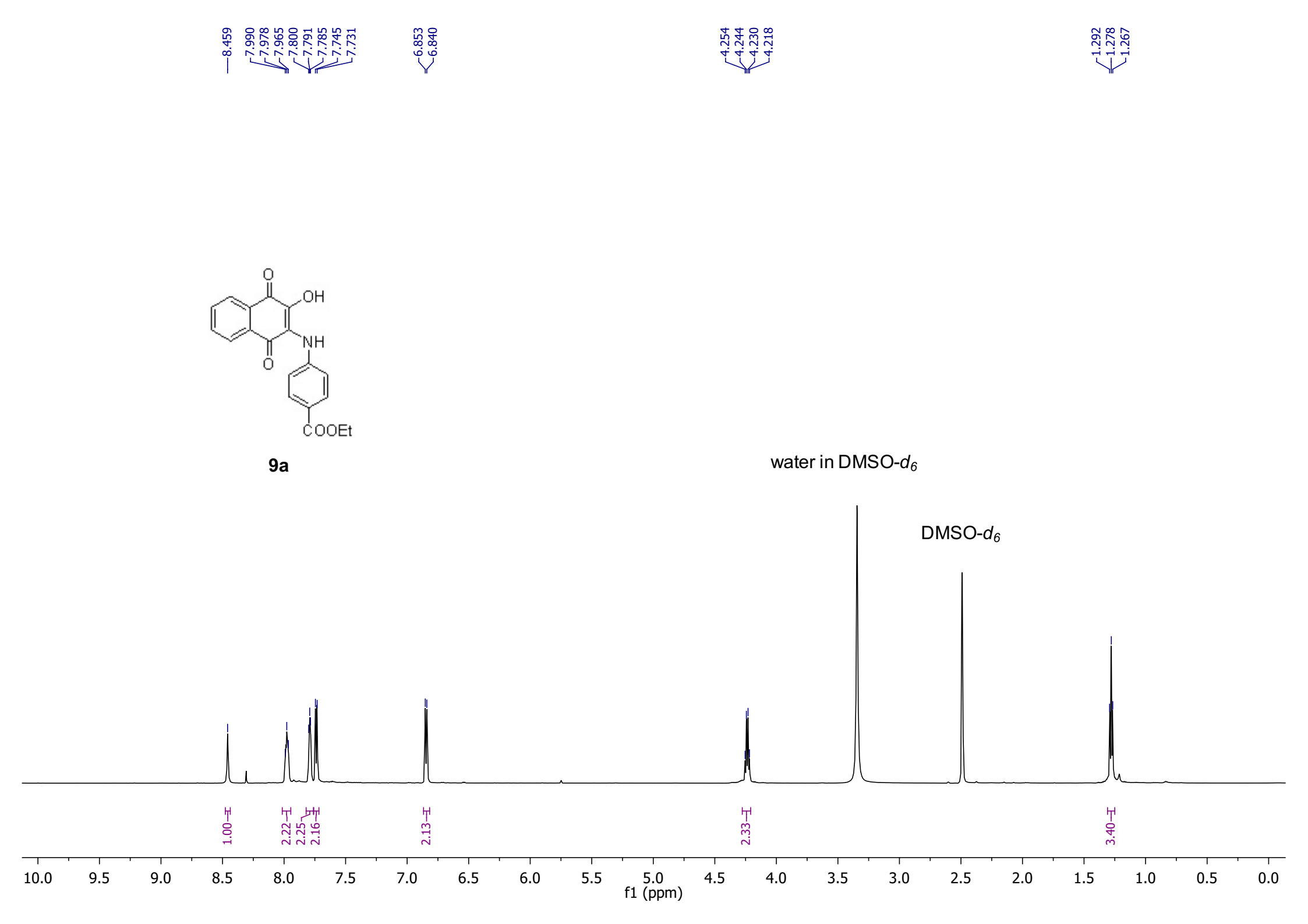
7c

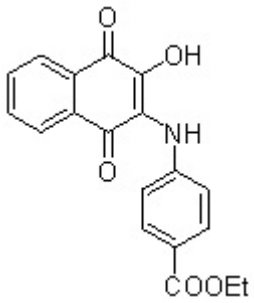

10.236
8.709
8.700
8.327
8.162
8.148
7.901
7.885
7.558
7.543
7.451
7.444
7.437
7.423
7.351
7.337
7.324
7.244
6.907
6.894
water in DMSO-d_6
DMSO-d_6
NO2
NH
OH
N
0.96
1.00
1.08
1.02
1.03
0.99
2.06
1.04
0.92
0.99
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

7d


151.22
148.84
148.79
147.58
143.63
130.57
130.19
128.51
127.14
122.40
121.74
119.80
118.35
111.50
106.93
NO2
NH
OH
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

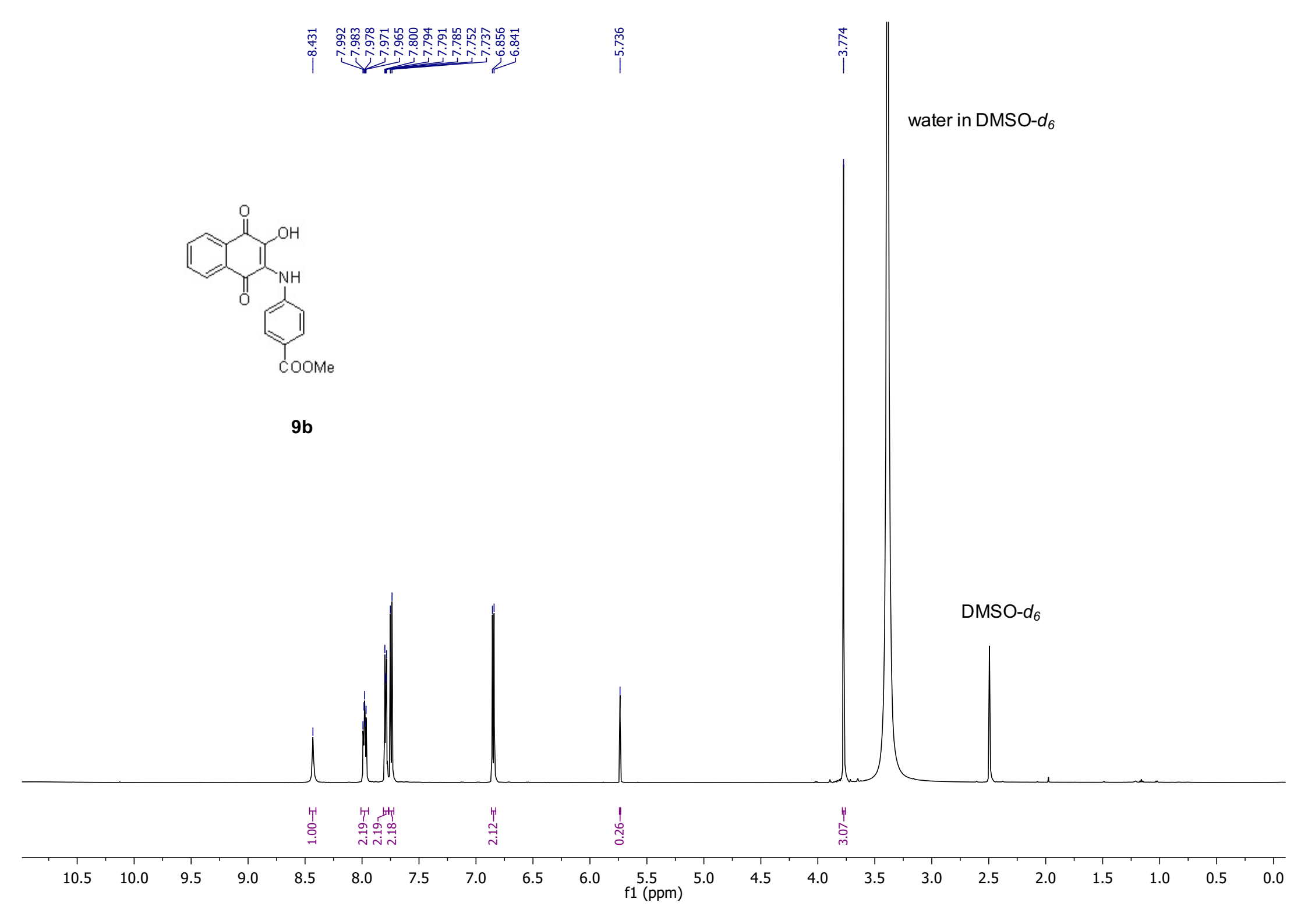
7d


8.459
7.990
7.978
7.965
7.800
7.791
7.785
7.745
7.731
6.853
6.840
4.254
4.244
4.230
4.218
1.292
1.278
1.267
O
OH
NH
O
COOEt
9a
water in DMSO-d_6
DMSO-d_6
1.00
2.22
2.25
2.16
2.13
2.33
3.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

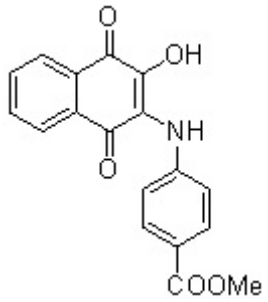

O
OH
NH
O
COOEt

9a

181.84
179.99
165.75
146.70
145.01
133.99
133.74
131.04
130.47
129.52
125.83
125.59
123.99
120.08
117.32
60.02
14.36
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

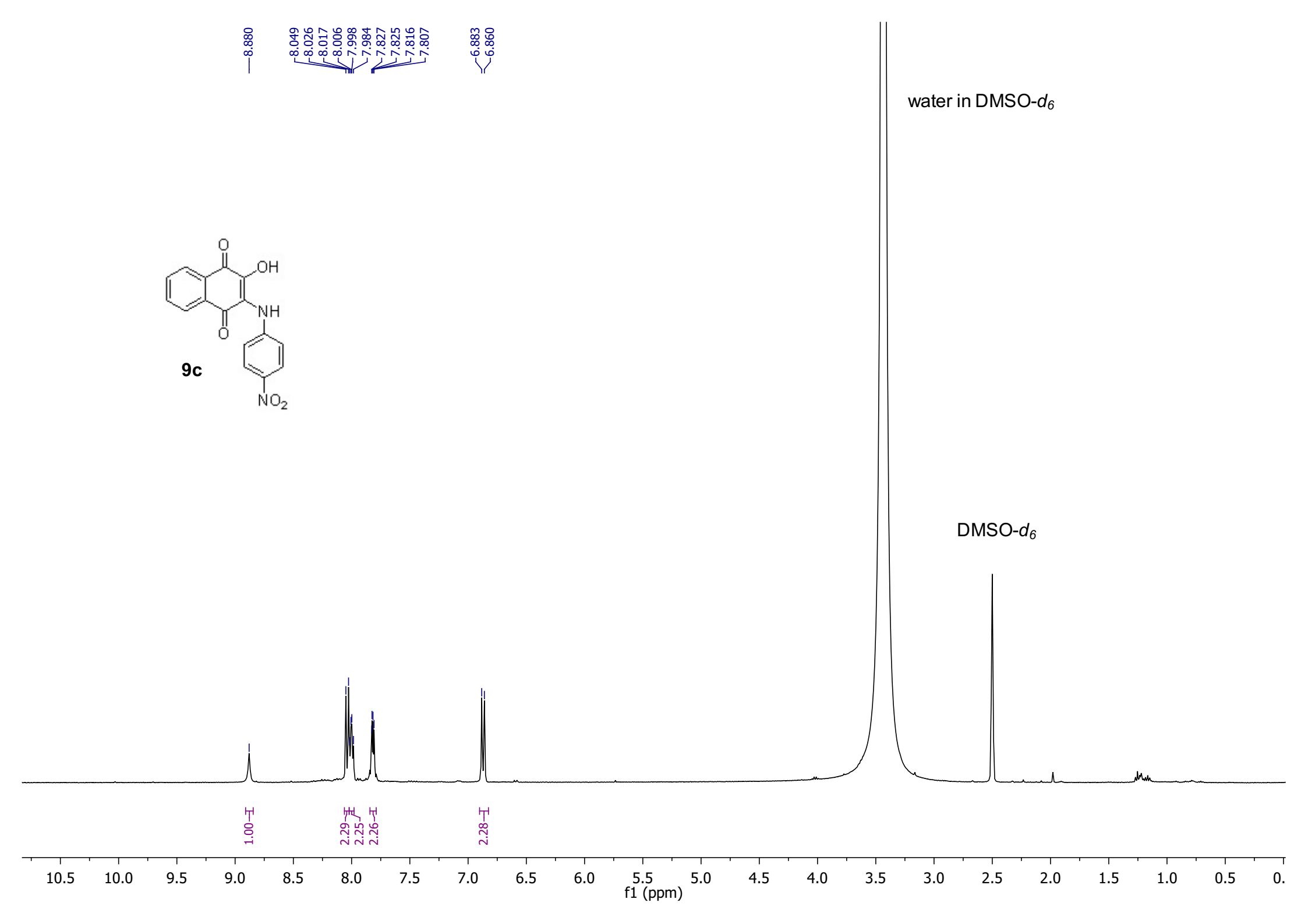

8.431
7.992
7.983
7.978
7.971
7.965
7.800
7.794
7.791
7.785
7.752
7.737
6.856
6.841
5.736
3.774
water in DMSO-d_6
DMSO-d_6
O
OH
NH
O
COOMe
1.00
2.19
2.19
2.18
2.12
0.26
3.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

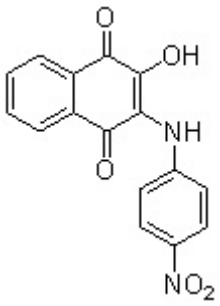
9b


O
OH
NH
O
COOMe

9b

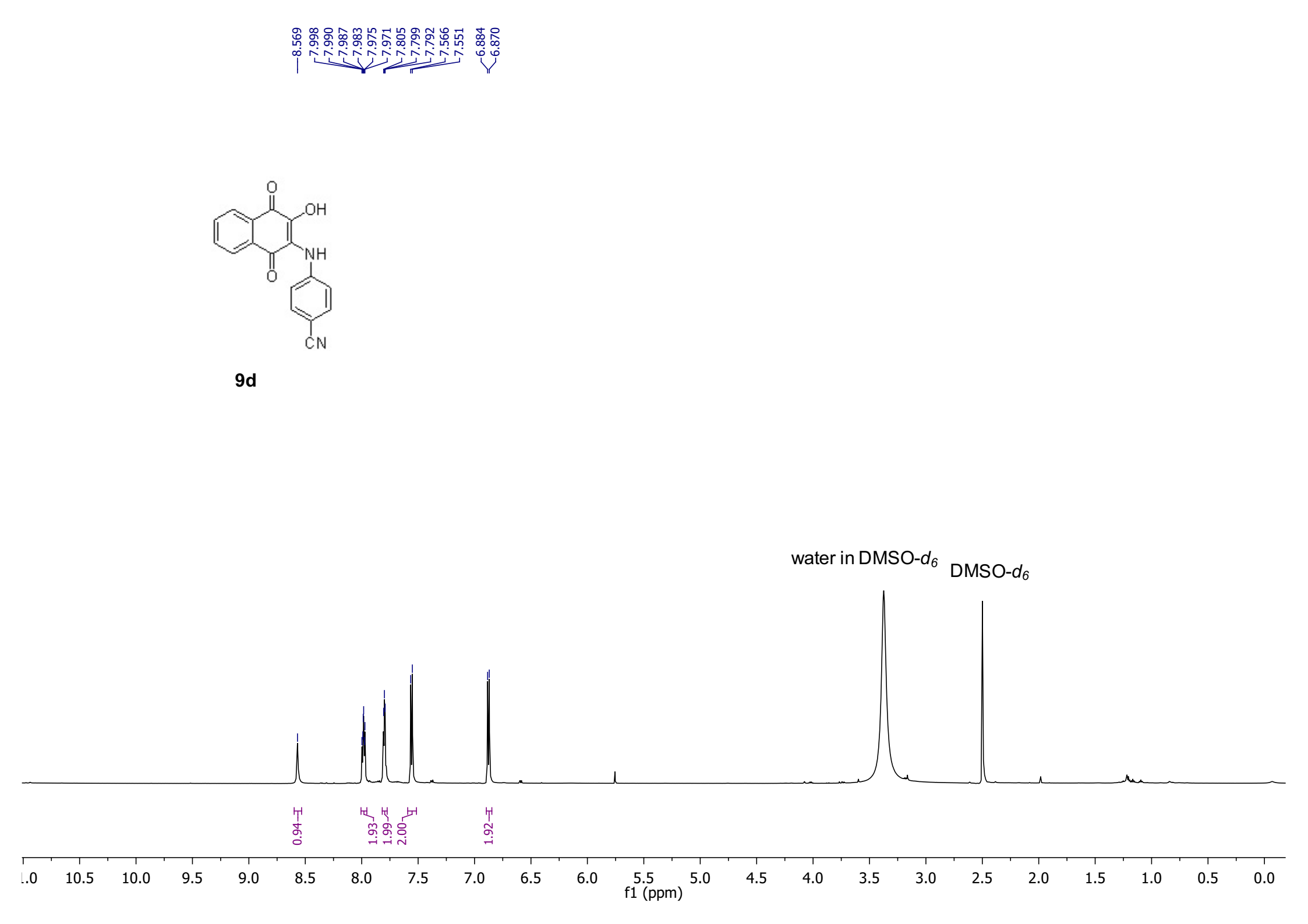
181.86
180.03
166.29
146.83
145.15
134.03
133.77
131.06
130.48
129.62
125.86
125.62
123.98
119.82
117.31
51.63
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.880
8.049
8.026
8.017
8.006
7.998
7.984
7.827
7.825
7.816
7.807
6.883
6.860
water in DMSO-d_6
DMSO-d_6
O
OH
NH
O
NO_2
9c
1.00
2.29
2.25
2.26
2.28
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

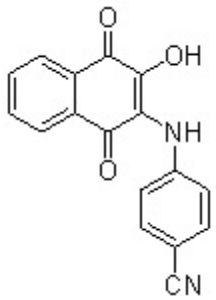

O
OH
NH
O
NO2

9c

181.89
180.84
149.92
148.05
138.89
134.67
134.11
131.62
130.84
126.32
126.15
125.11
123.11
116.80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

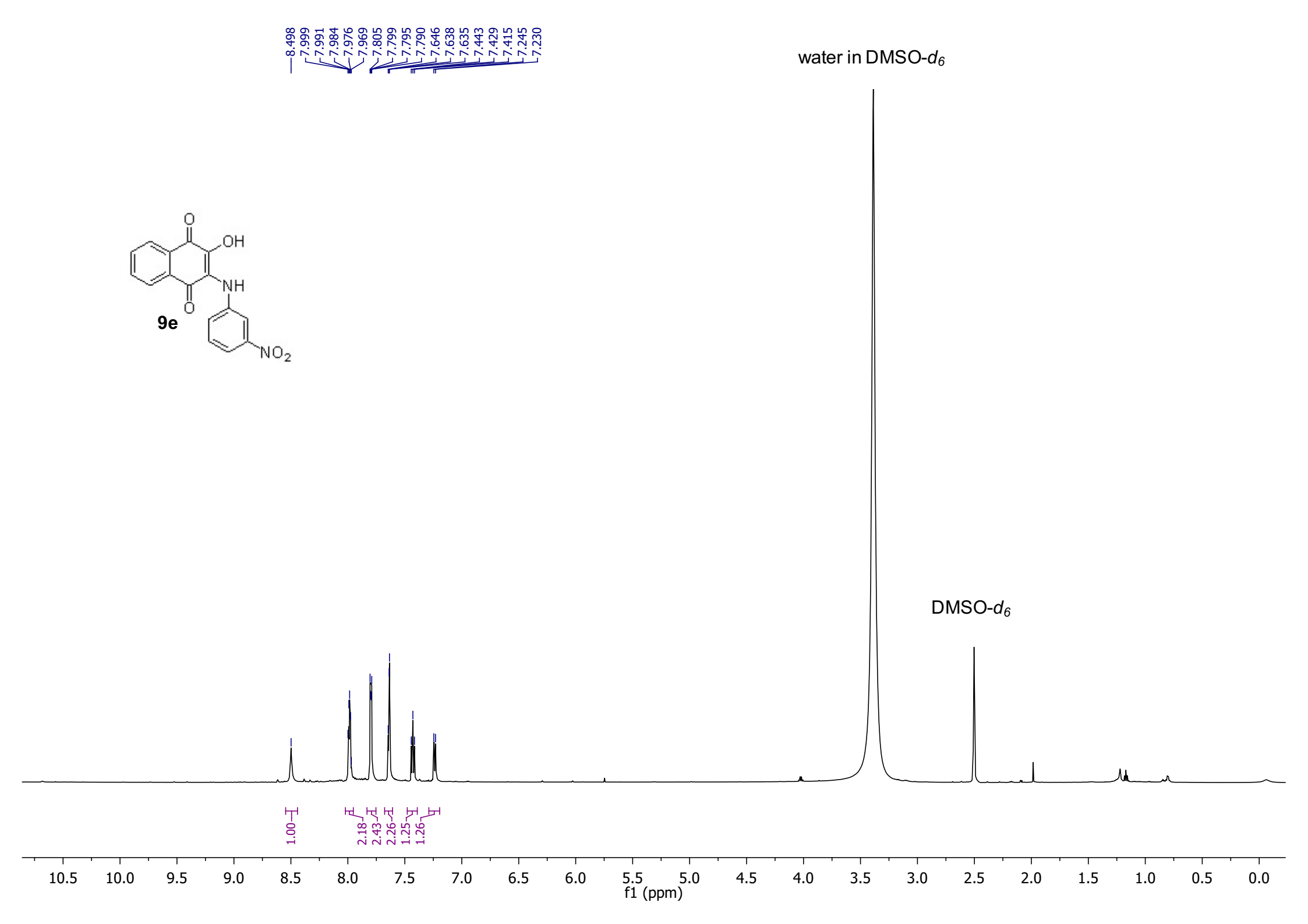

8.569
7.998
7.990
7.987
7.983
7.975
7.971
7.805
7.799
7.792
7.566
7.551
6.884
6.870
O
OH
NH
O
CN
water in DMSO-d_6
DMSO-d_6
0.94
1.93
1.99
2.00
1.92
f1 (ppm)

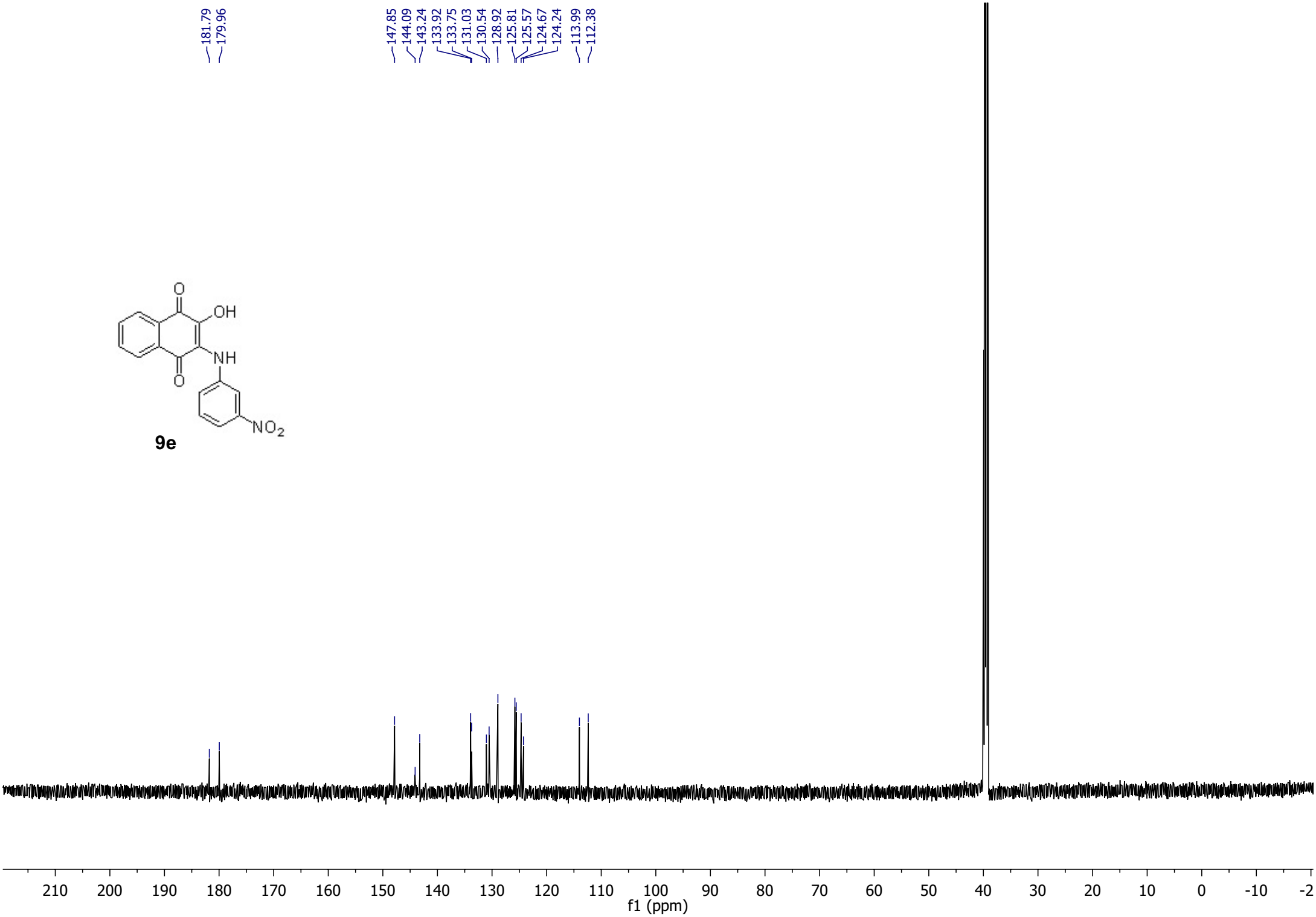
9d

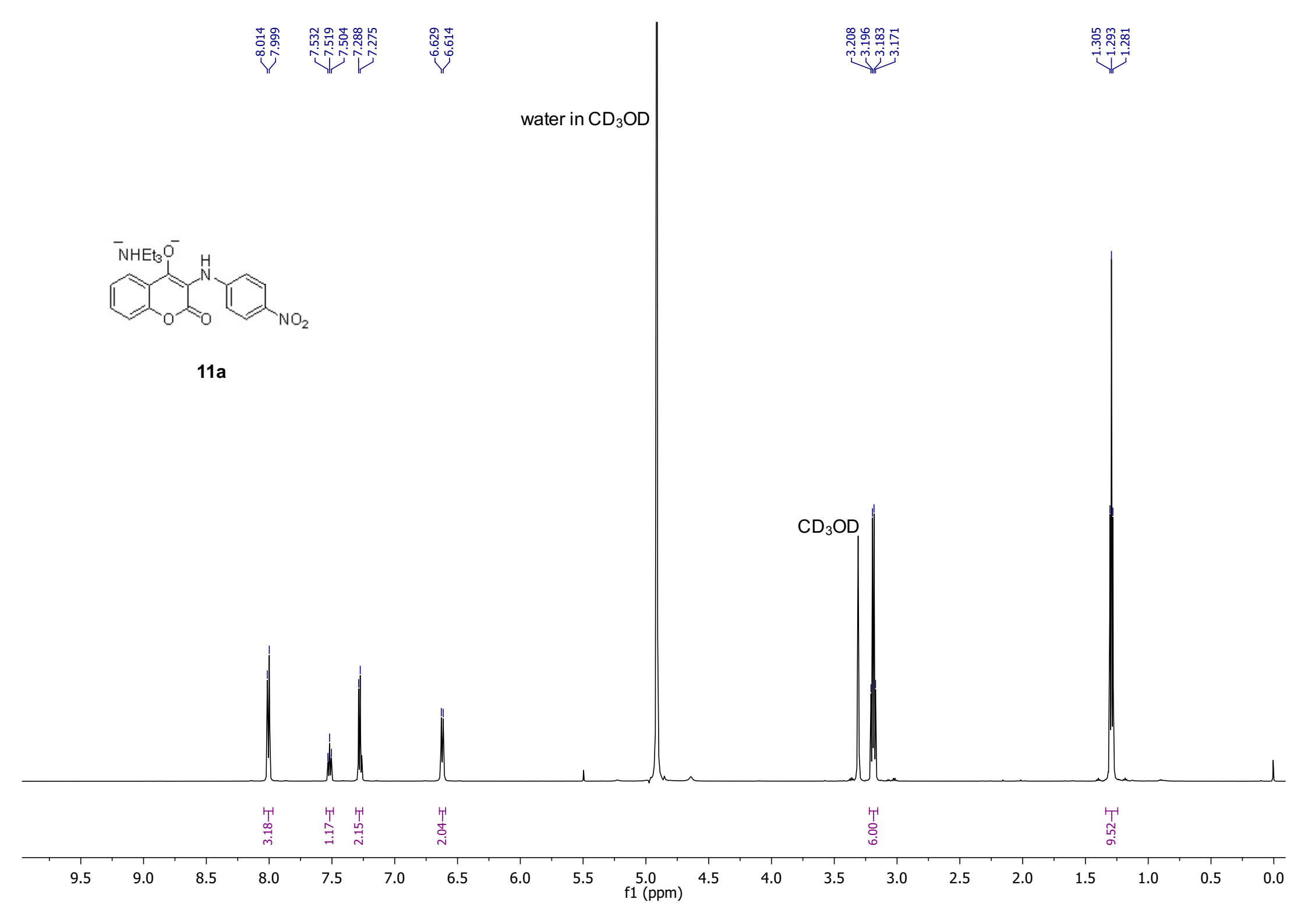

O
OH
NH
O
CN

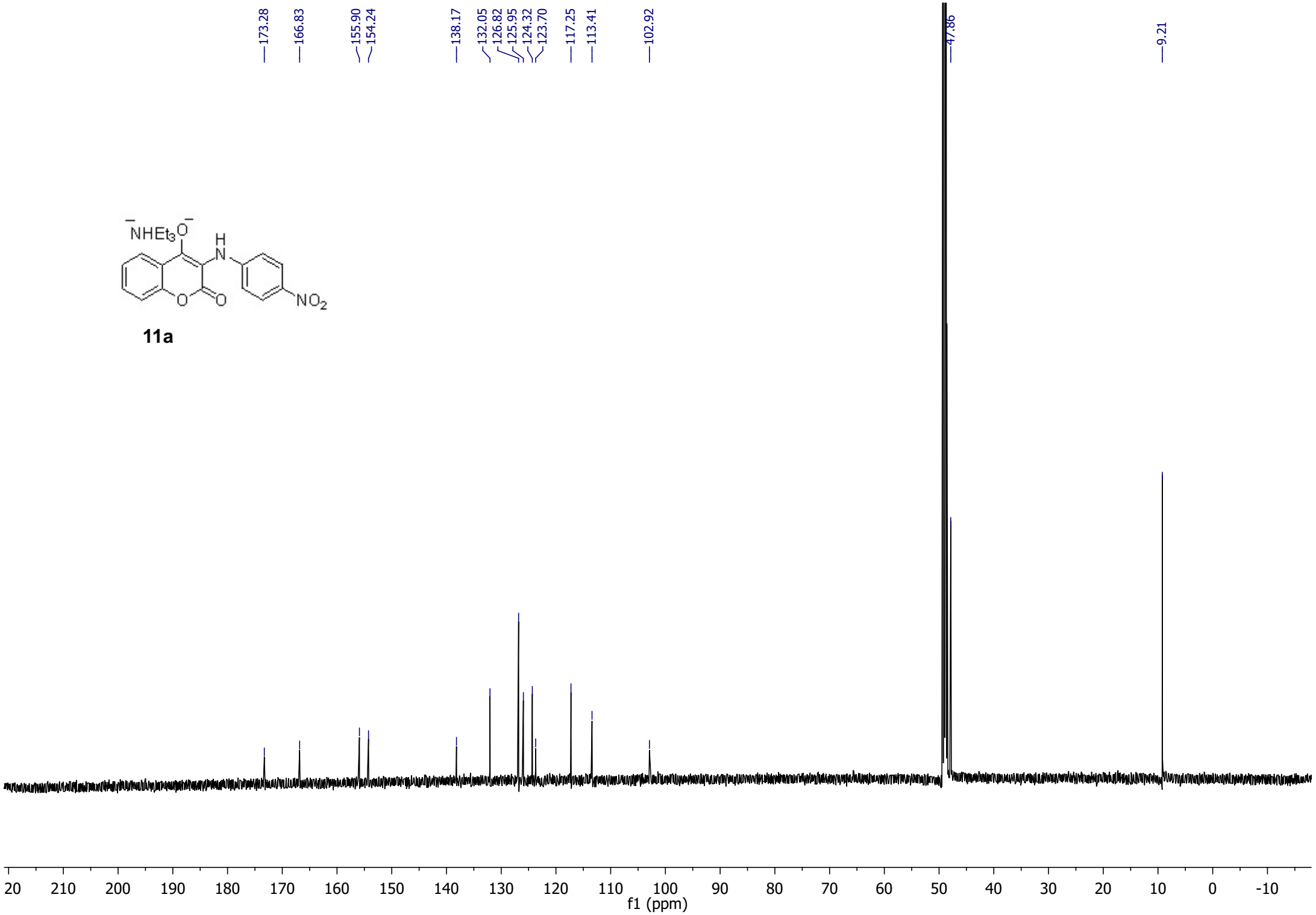
9d

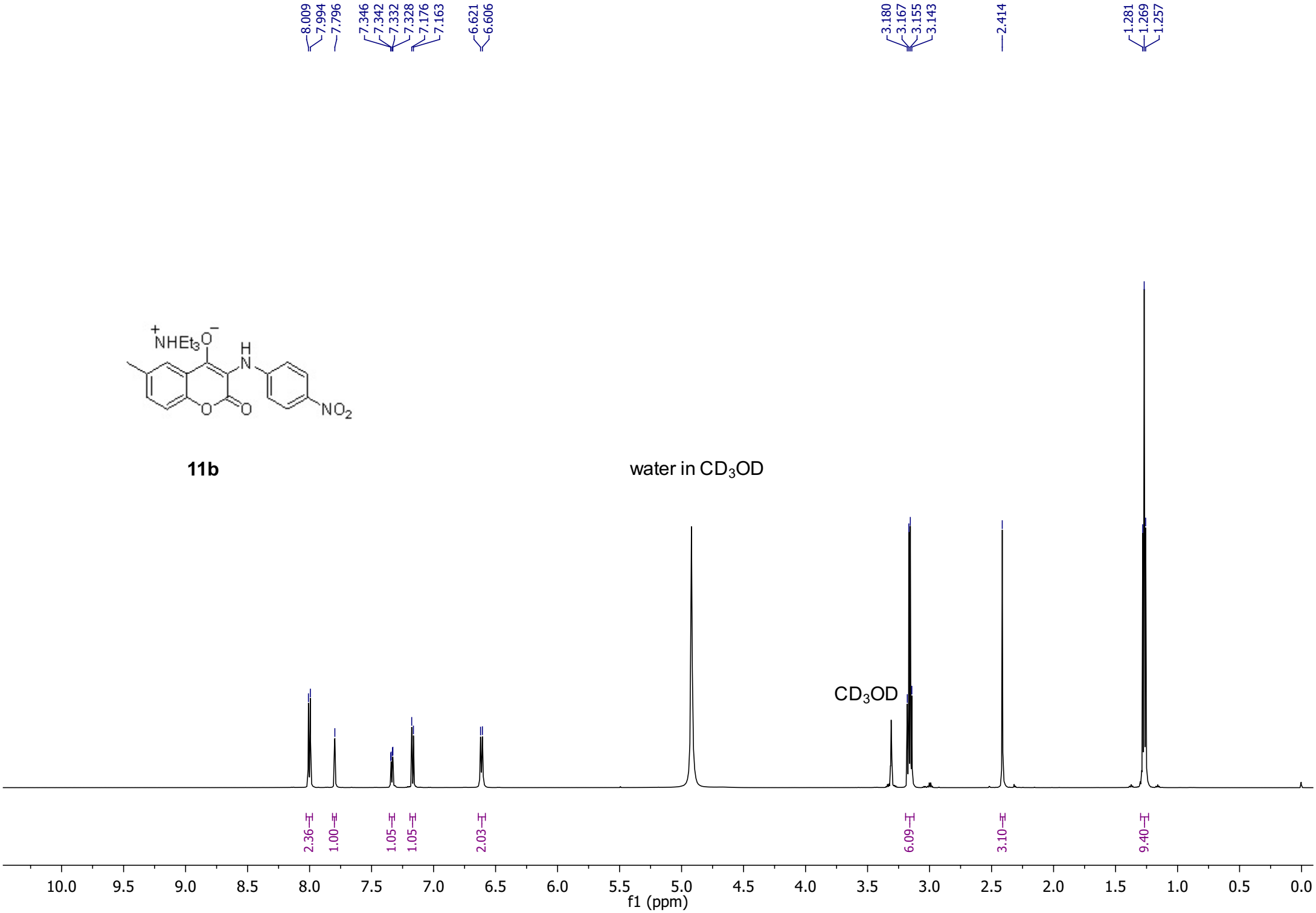
181.66
180.23
146.74
146.16
134.08
133.69
132.32
131.17
130.48
125.85
125.65
123.32
120.12
117.71
99.84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

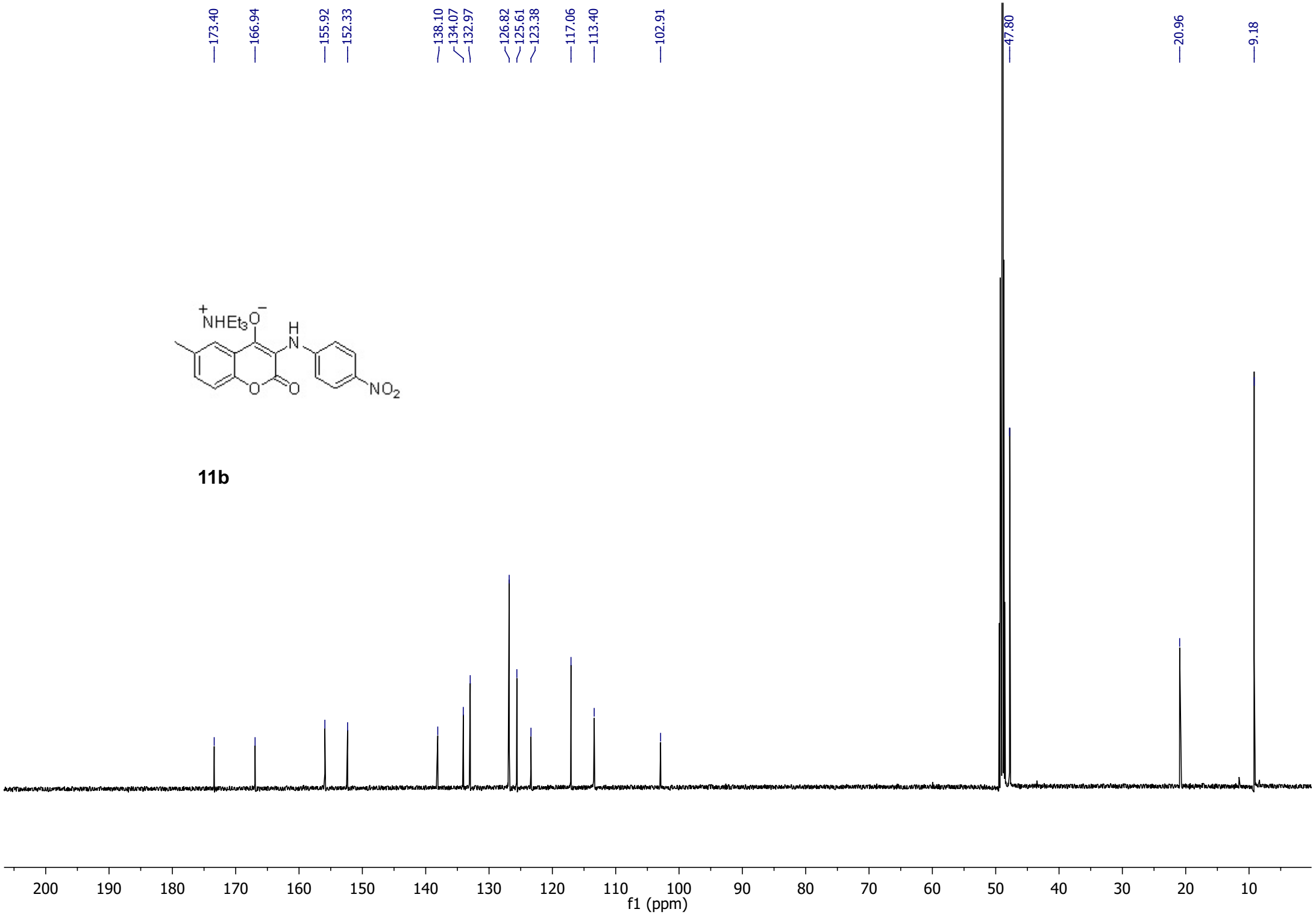

8.498
7.999
7.991
7.984
7.976
7.969
7.805
7.799
7.795
7.790
7.646
7.638
7.635
7.443
7.429
7.415
7.245
7.230
water in DMSO-d_6
DMSO-d_6
O
OH
NH
O
NO_2
9e
1.00
2.18
2.43
2.26
1.25
1.26
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


181.79
179.96
147.85
144.09
143.24
133.92
133.75
131.03
130.54
128.92
125.81
125.57
124.67
124.24
113.99
112.38
O
OH
NH
O
NO2
9e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

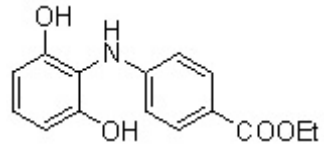

8.014
7.999
7.532
7.519
7.504
7.288
7.275
6.629
6.614
3.208
3.196
3.183
3.171
1.305
1.293
1.281
water in CD3OD
CD3OD
NHEt3
O
H
N
O
O
NO2
11a
3.18
1.17
2.15
2.04
6.00
9.52
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.28
166.83
155.90
154.24
138.17
132.05
126.82
125.95
124.32
123.70
117.25
113.41
102.92
47.86
9.21
NHEt3
O
H
N
O
O
NO2
11a
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.009
7.994
7.796
7.346
7.342
7.332
7.328
7.176
7.163
6.621
6.606
3.180
3.167
3.155
3.143
2.414
1.281
1.269
1.257
NHEt3
O
H
N
O
O
NO2
11b
water in CD3OD
CD3OD
2.36
1.00
1.05
1.05
2.03
6.09
3.10
9.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

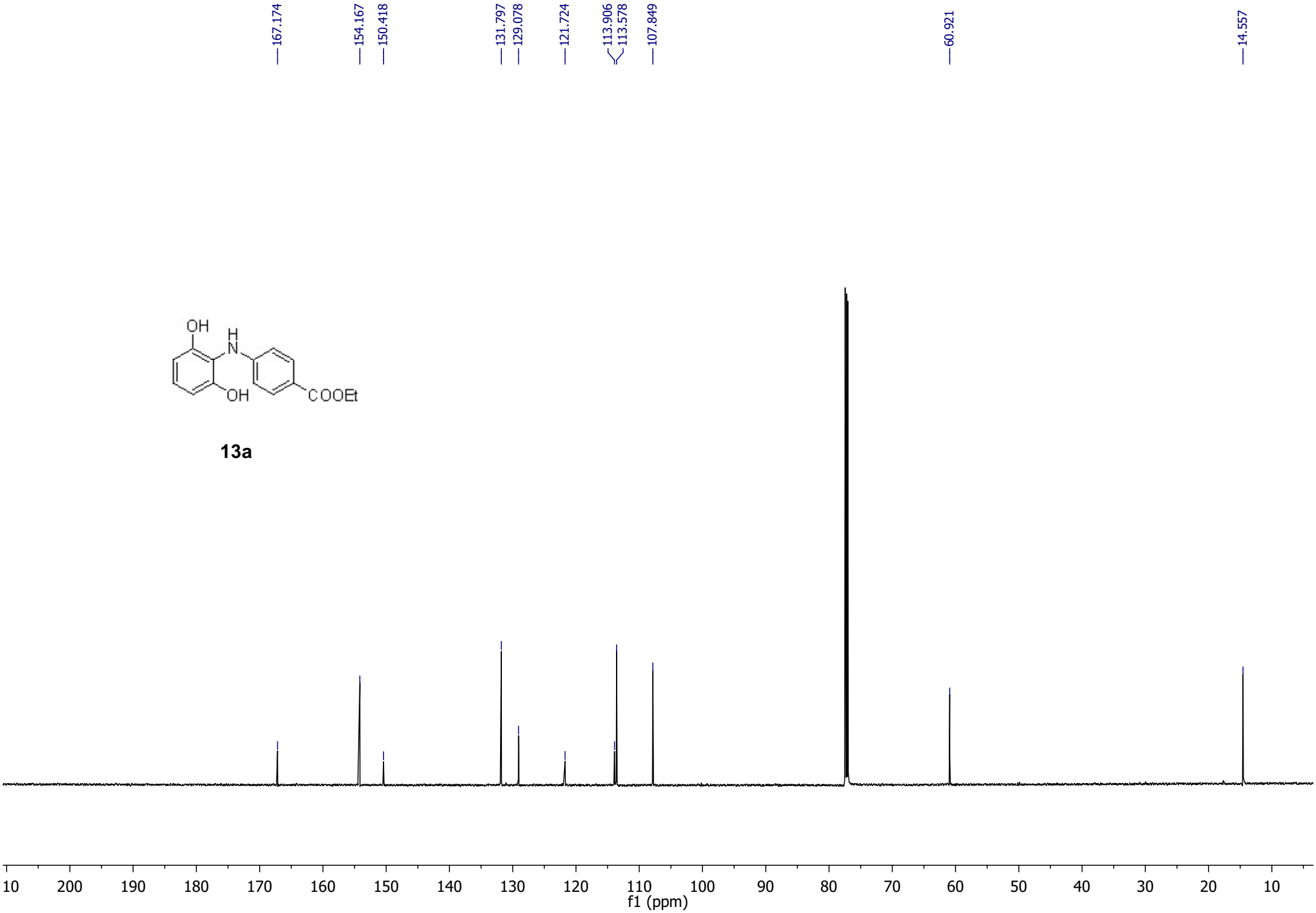

173.40
166.94
155.92
152.33
138.10
134.07
132.97
126.82
125.61
123.38
117.06
113.40
102.91
47.80
20.96
9.18
NHEt3
O
H
N
O
O
NO2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

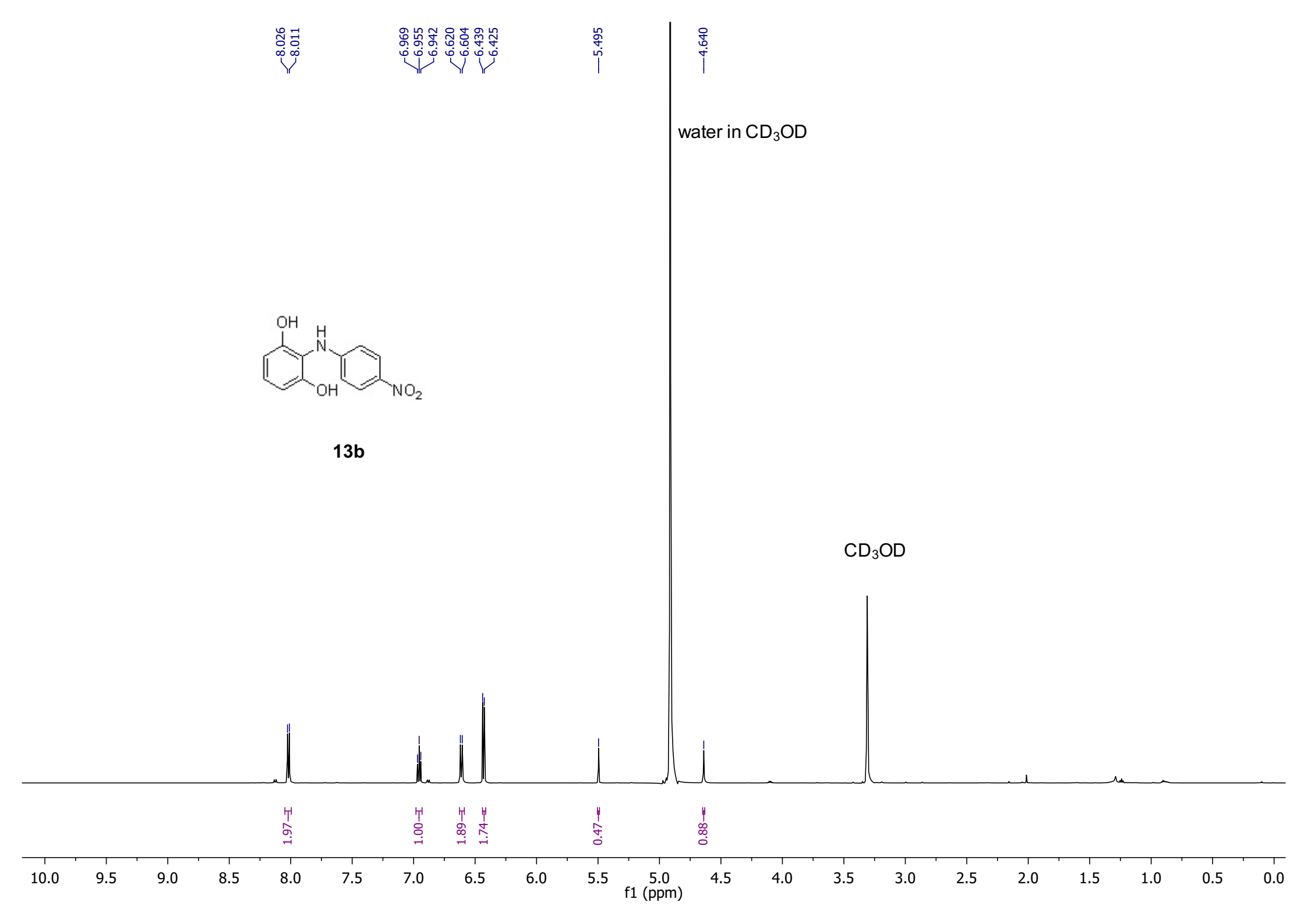
11b

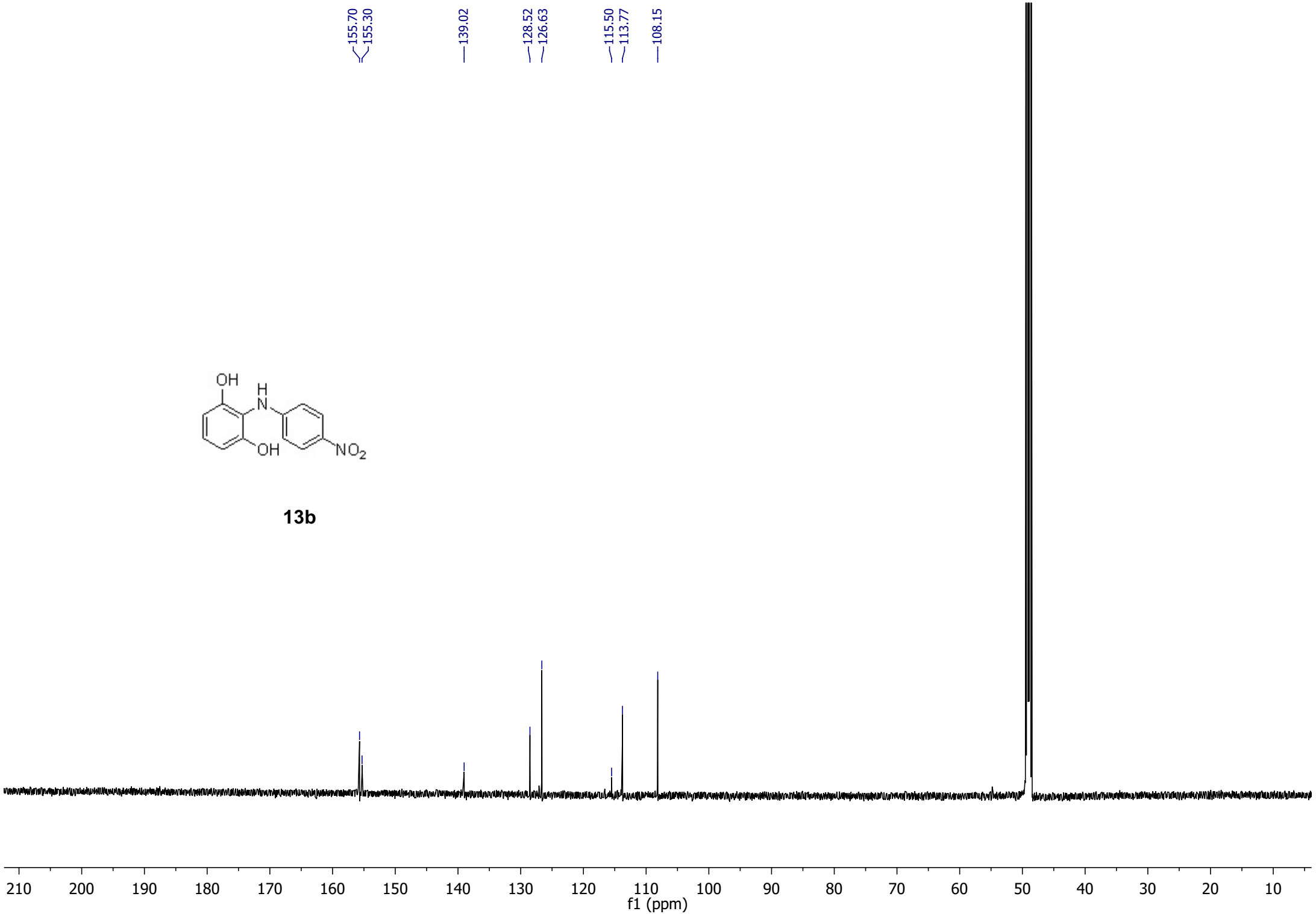

OH
H
N
OH
COOEt

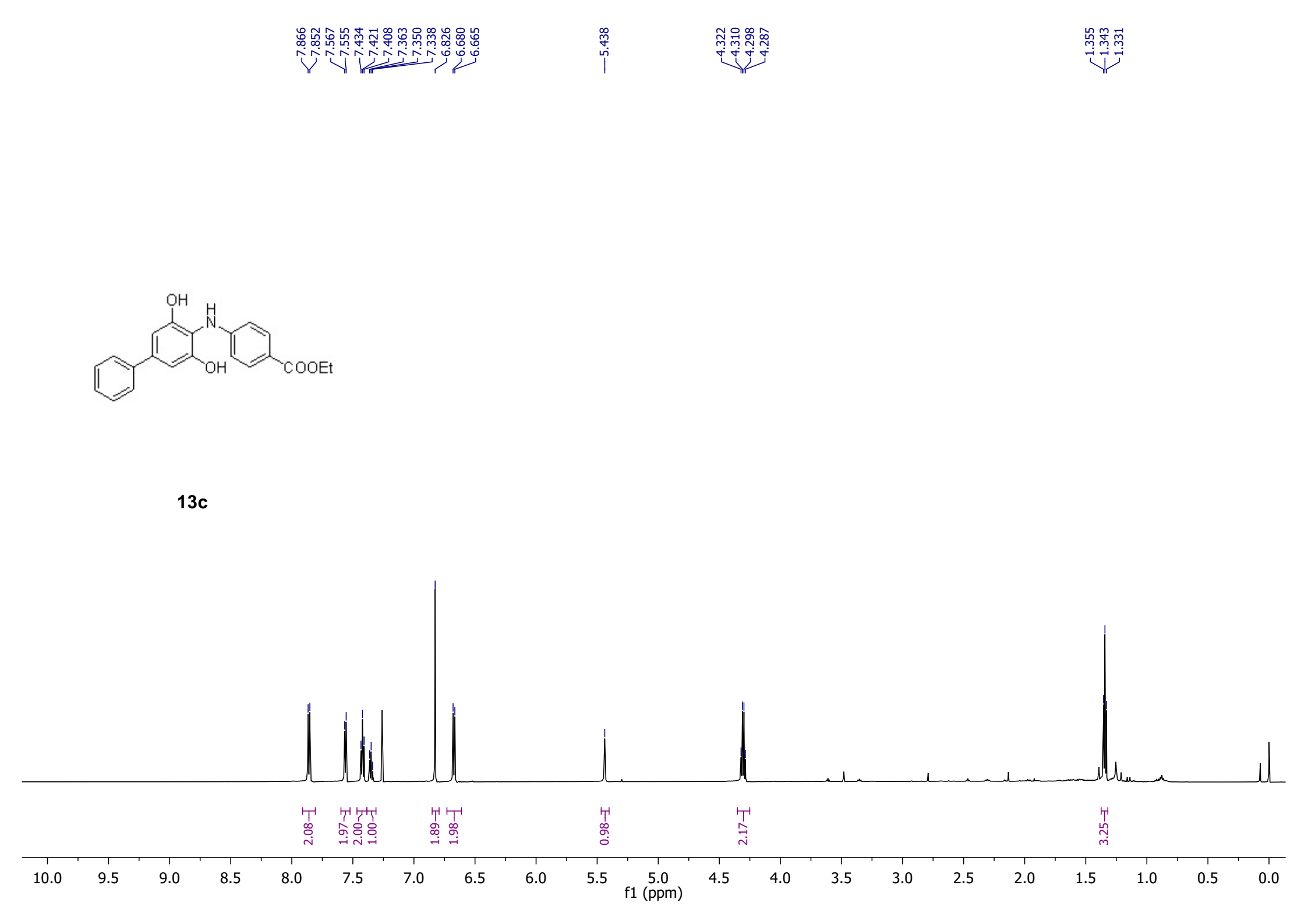
13a

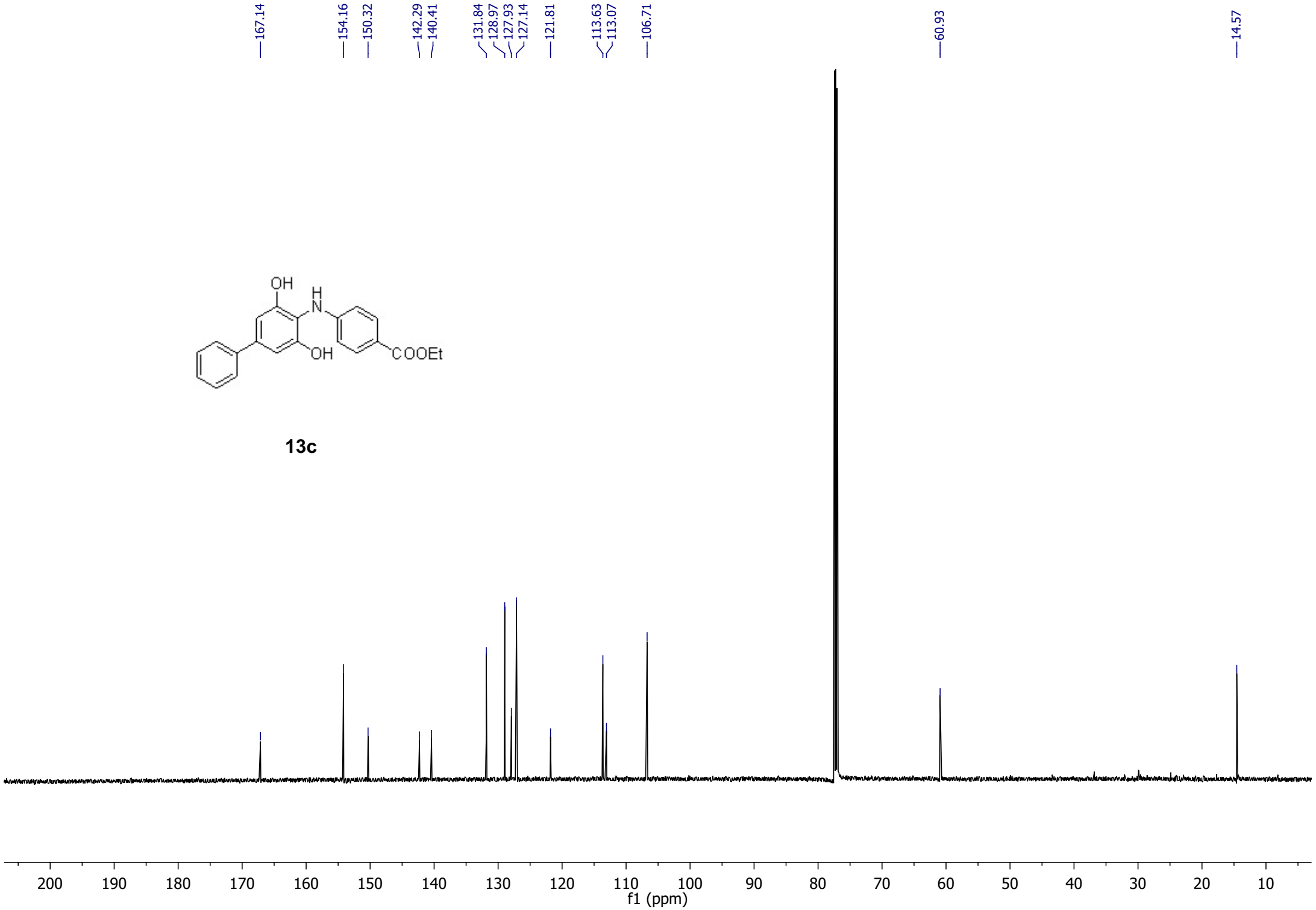
7.841
7.826
7.108
7.094
7.081
6.626
6.611
6.577
6.563
5.410
4.315
4.303
4.292
4.280
1.353
1.341
1.329
1.97
1.00
2.03
1.91
0.93
2.18
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

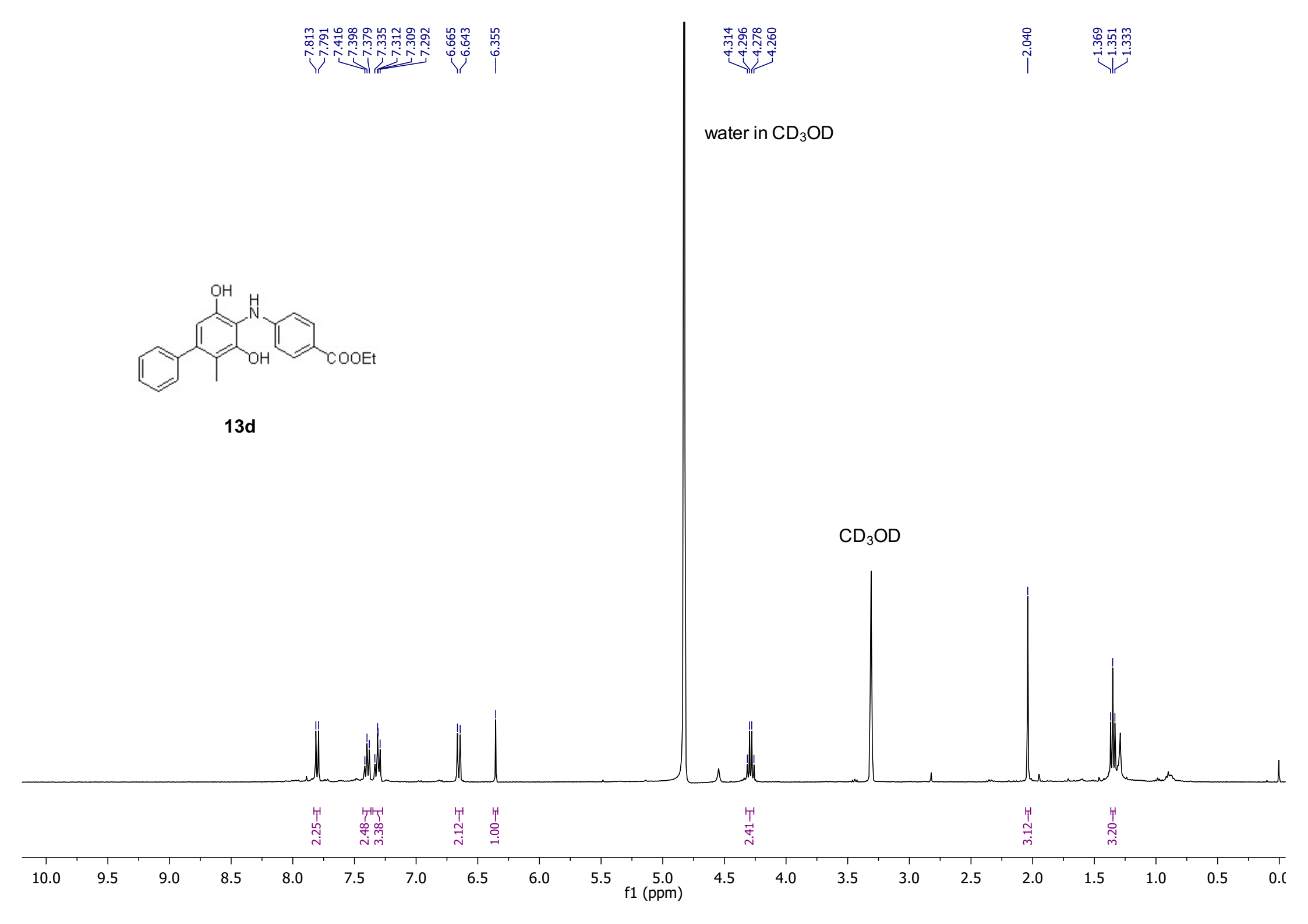

167.174
154.167
150.418
131.797
129.078
121.724
113.906
113.578
107.849
60.921
14.557
OH
H
N
OH
COOEt
13a
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

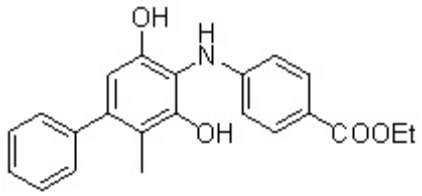

8.026
8.011
6.969
6.955
6.942
6.620
6.604
6.439
6.425
5.495
4.640
water in CD3OD
CD3OD
OH
H
N
OH
NO2
13b
1.97
1.00
1.89
1.74
0.47
0.88
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.70
155.30
139.02
128.52
126.63
115.50
113.77
108.15
OH
H
N
OH
NO2
13b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.866
7.852
7.567
7.555
7.434
7.421
7.408
7.363
7.350
7.338
6.826
6.680
6.665
5.438
4.322
4.310
4.298
4.287
1.355
1.343
1.331
OH
H
N
OH
COOEt
13c
2.08
1.97
2.00
1.00
1.89
1.98
0.98
2.17
3.25
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

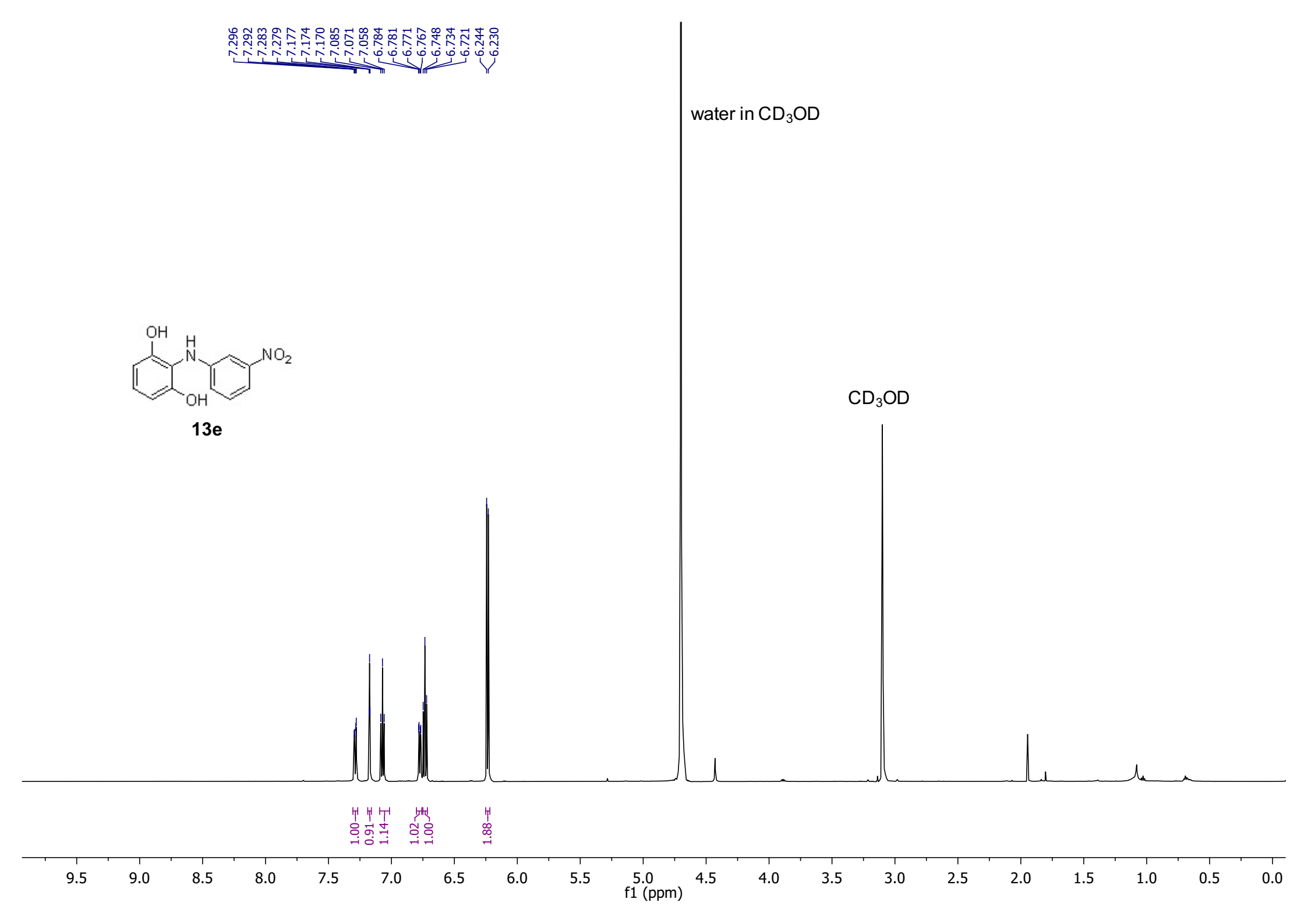

167.14
154.16
150.32
142.29
140.41
131.84
128.97
127.93
127.14
121.81
113.63
113.07
106.71
60.93
14.57
OH
H
N
OH
COOEt
13c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

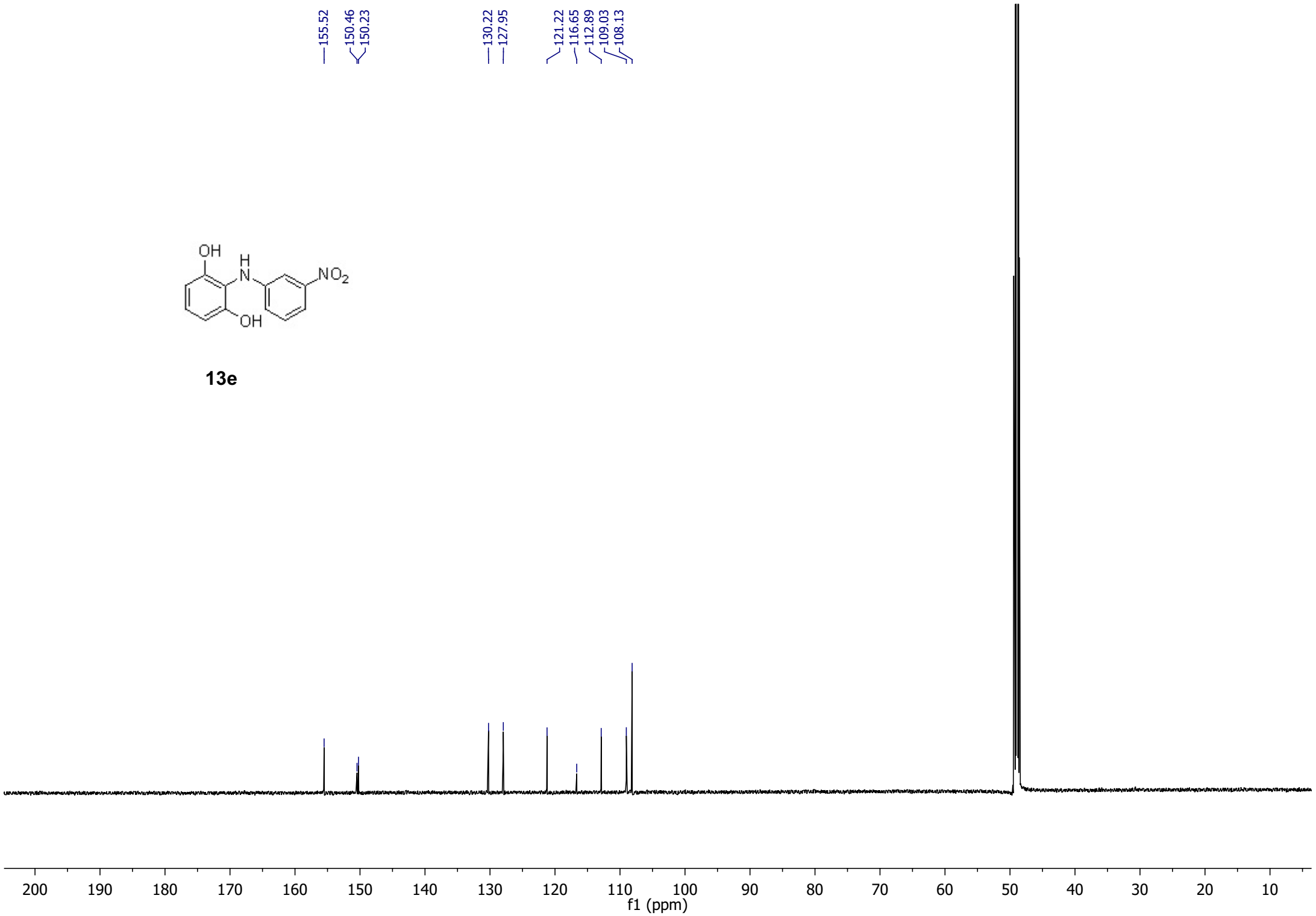

7.813
7.791
7.416
7.398
7.379
7.335
7.312
7.309
7.292
6.665
6.643
6.355
4.314
4.296
4.278
4.260
2.040
1.369
1.351
1.333
water in CD3OD
CD3OD
OH
H
N
OH
COOEt
13d
2.25
2.48
3.38
2.12
1.00
2.41
3.12
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

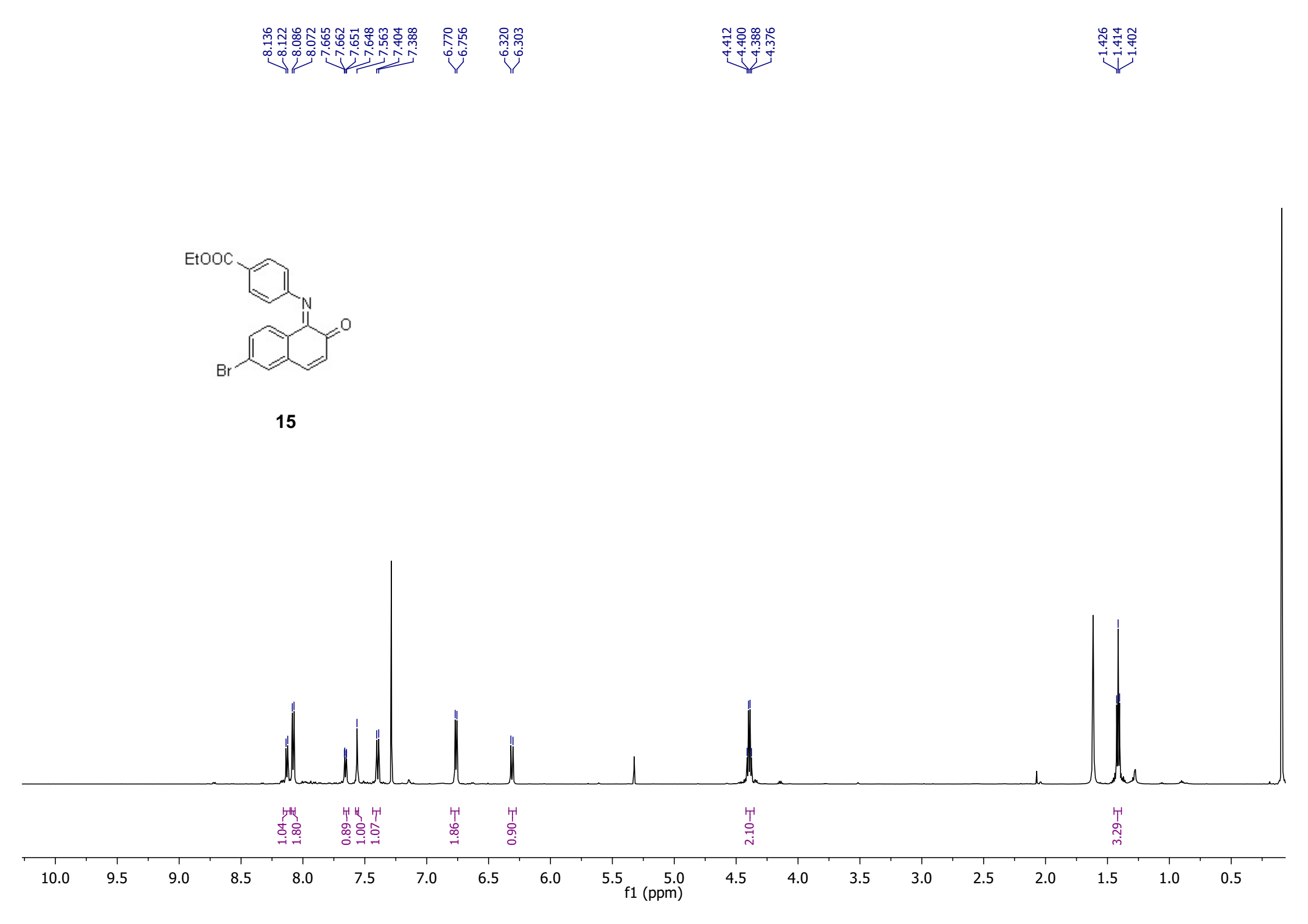

OH
H
N
OH
COOEt

13d

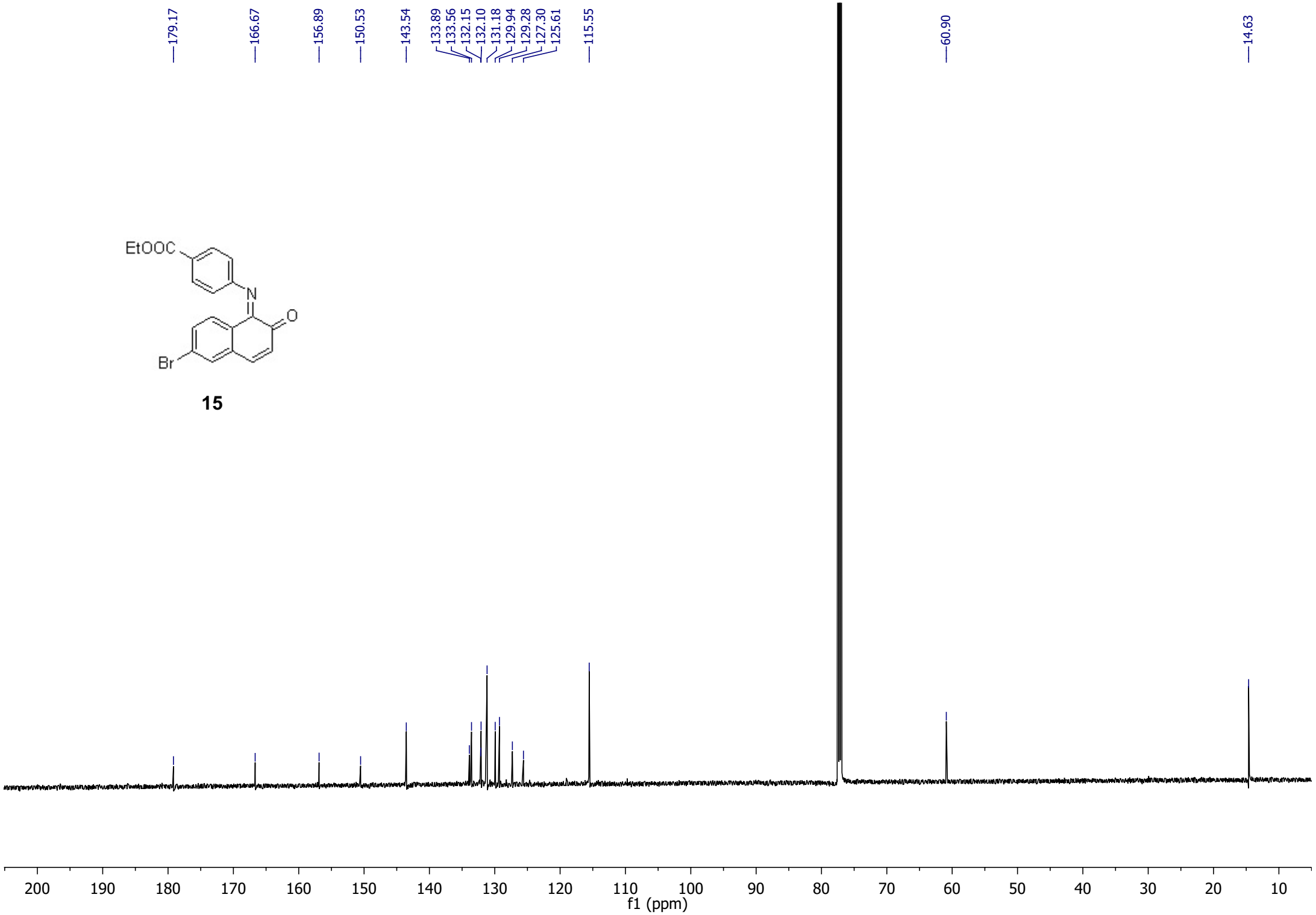
168.86
154.13
153.70
152.79
143.53
142.94
132.04
130.21
129.02
127.77
120.09
115.05
114.61
114.18
109.38
61.40
14.71
13.39
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.296
7.292
7.283
7.279
7.177
7.174
7.170
7.085
7.071
7.058
6.784
6.781
6.771
6.767
6.748
6.734
6.721
6.244
6.230
water in CD3OD
CD3OD
OH
H
N
NO2
OH
13e
1.00
0.91
1.14
1.02
1.00
1.88
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

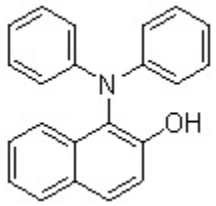

155.52
150.46
150.23
130.22
127.95
121.22
116.65
112.89
109.03
108.13
OH
H
N
NO2
OH
13e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.136
8.122
8.086
8.072
7.665
7.662
7.651
7.648
7.563
7.404
7.388
6.770
6.756
6.320
6.303
4.412
4.400
4.388
4.376
1.426
1.414
1.402
EtOOC
N
O
Br
1.04
1.80
0.89
1.00
1.07
1.86
0.90
2.10
3.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

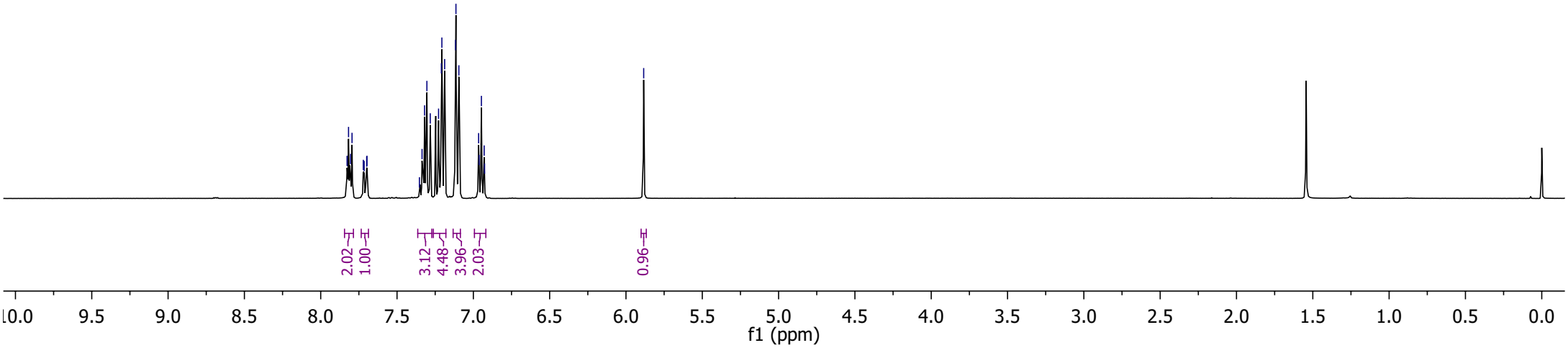
15

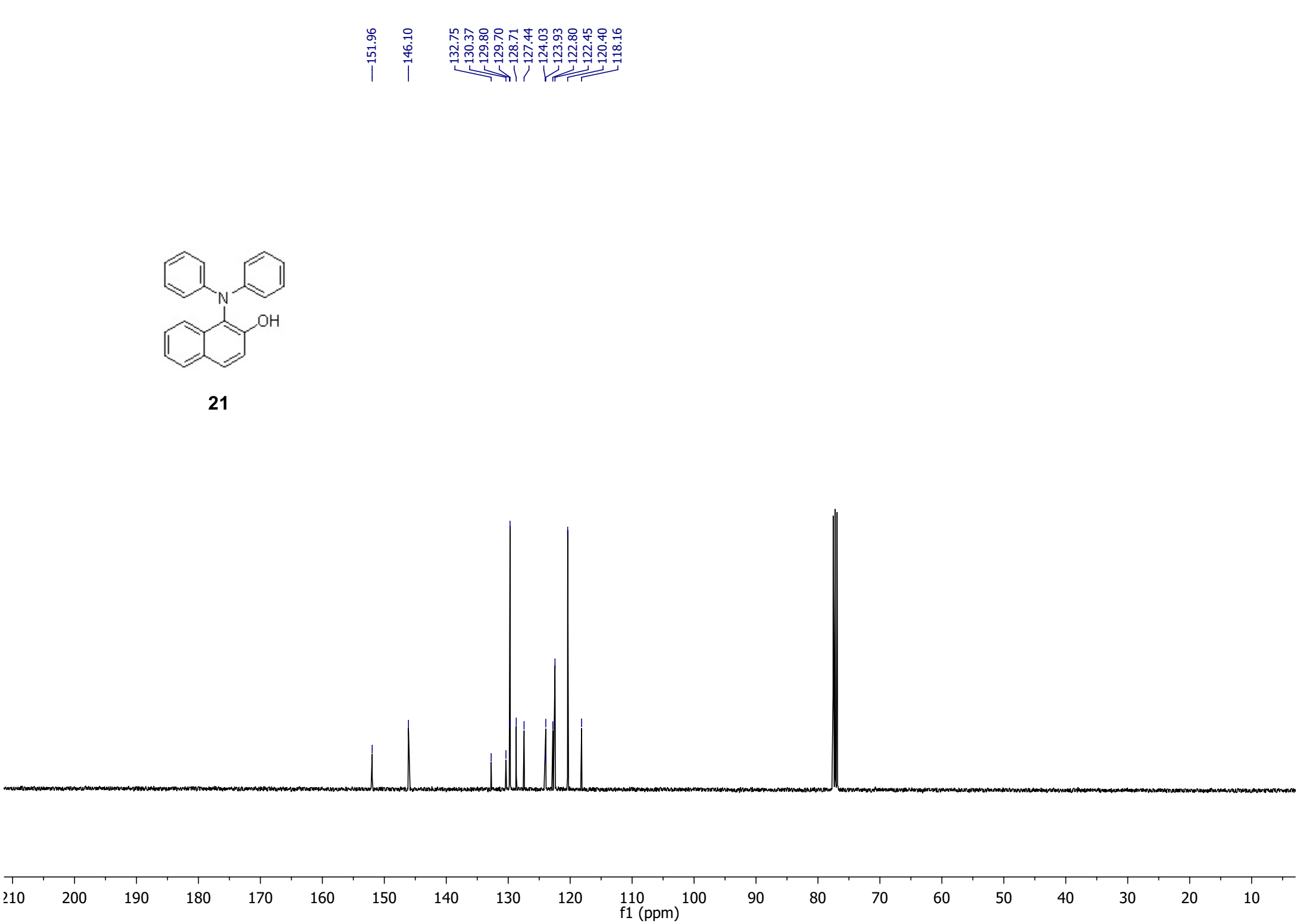

179.17
166.67
156.89
150.53
143.54
133.89
133.56
132.15
132.10
131.18
129.94
129.28
127.30
125.61
115.55
60.90
14.63
EtOOC
N
O
Br
15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.827
7.818
7.804
7.795
7.721
7.715
7.699
7.697
7.353
7.336
7.320
7.304
7.282
7.228
7.210
7.206
7.188
7.117
7.114
7.095
6.965
6.963
6.947
6.929
6.926
5.884

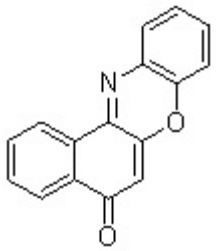

N
OH

21

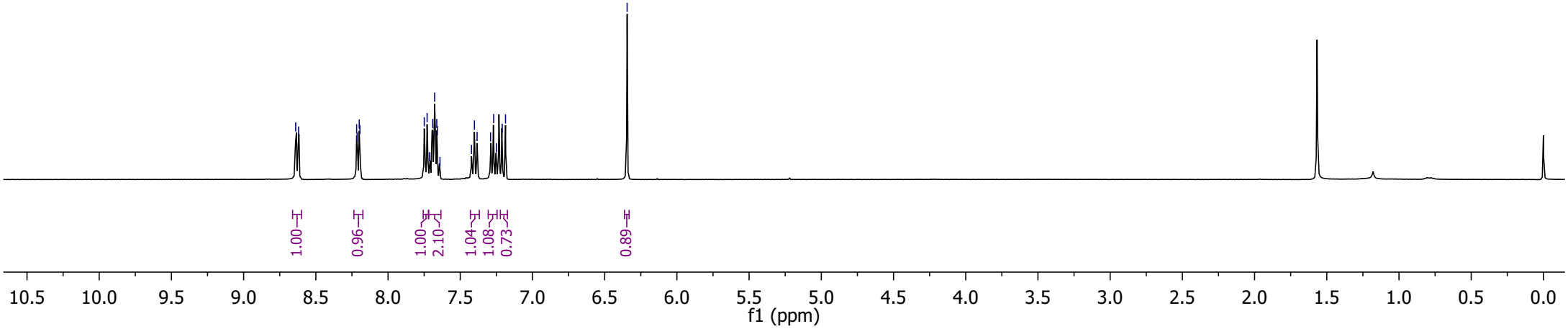

2.02
1.00
3.12
4.48
3.96
2.03
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

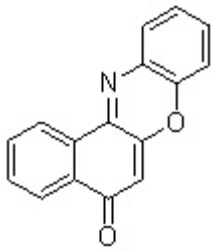

151.96
146.10
132.75
130.37
129.80
129.70
128.71
127.44
124.03
123.93
122.80
122.45
120.40
118.16
N
OH
21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.639
8.619
8.217
8.214
8.200
8.195
7.749
7.730
7.713
7.691
7.677
7.662
7.658
7.640
7.422
7.402
7.383
7.290
7.269
7.249
7.210
7.187
6.345


N
O
O

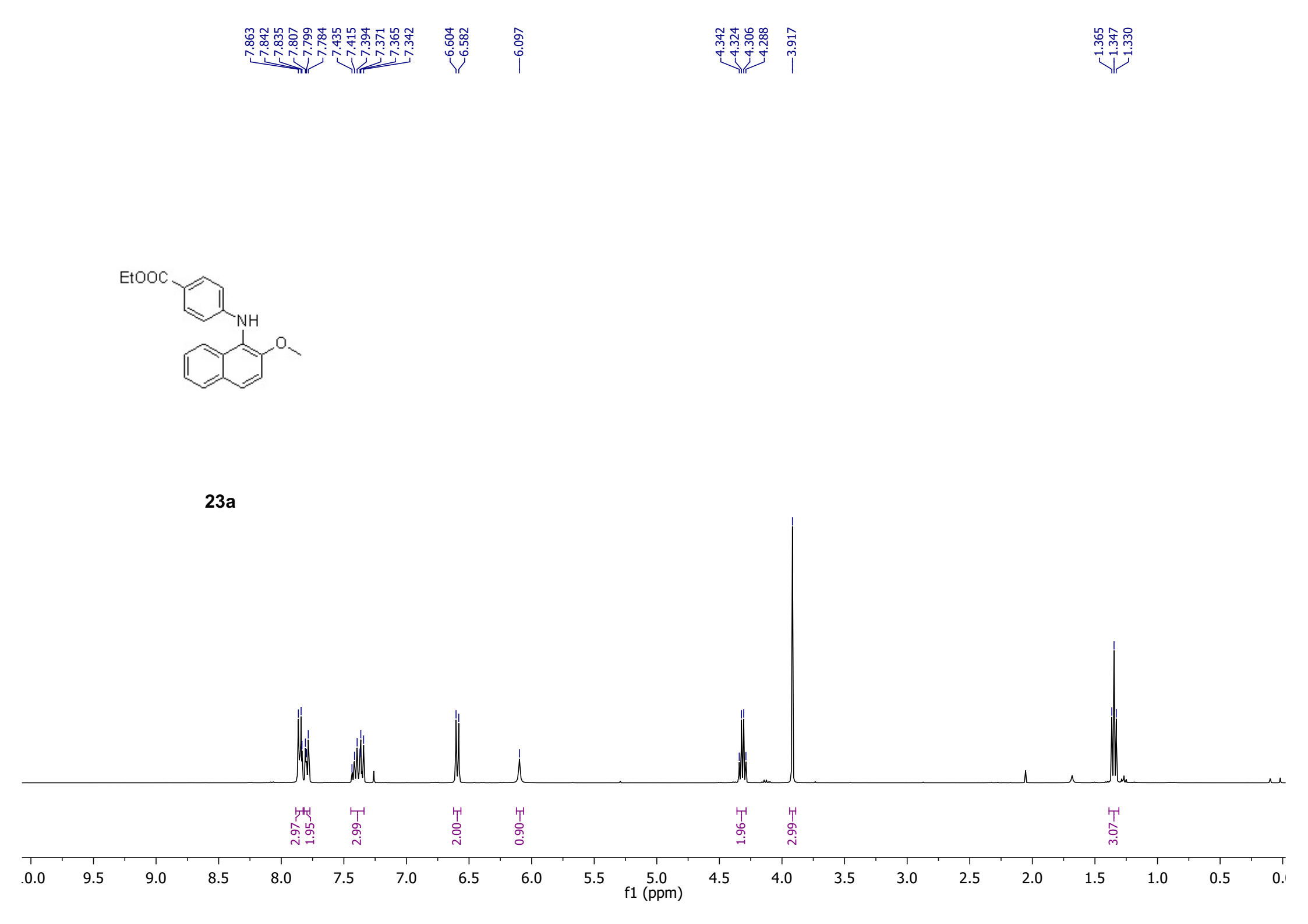
22


1.00
0.96
1.00
2.10
1.04
1.08
0.73
0.89
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

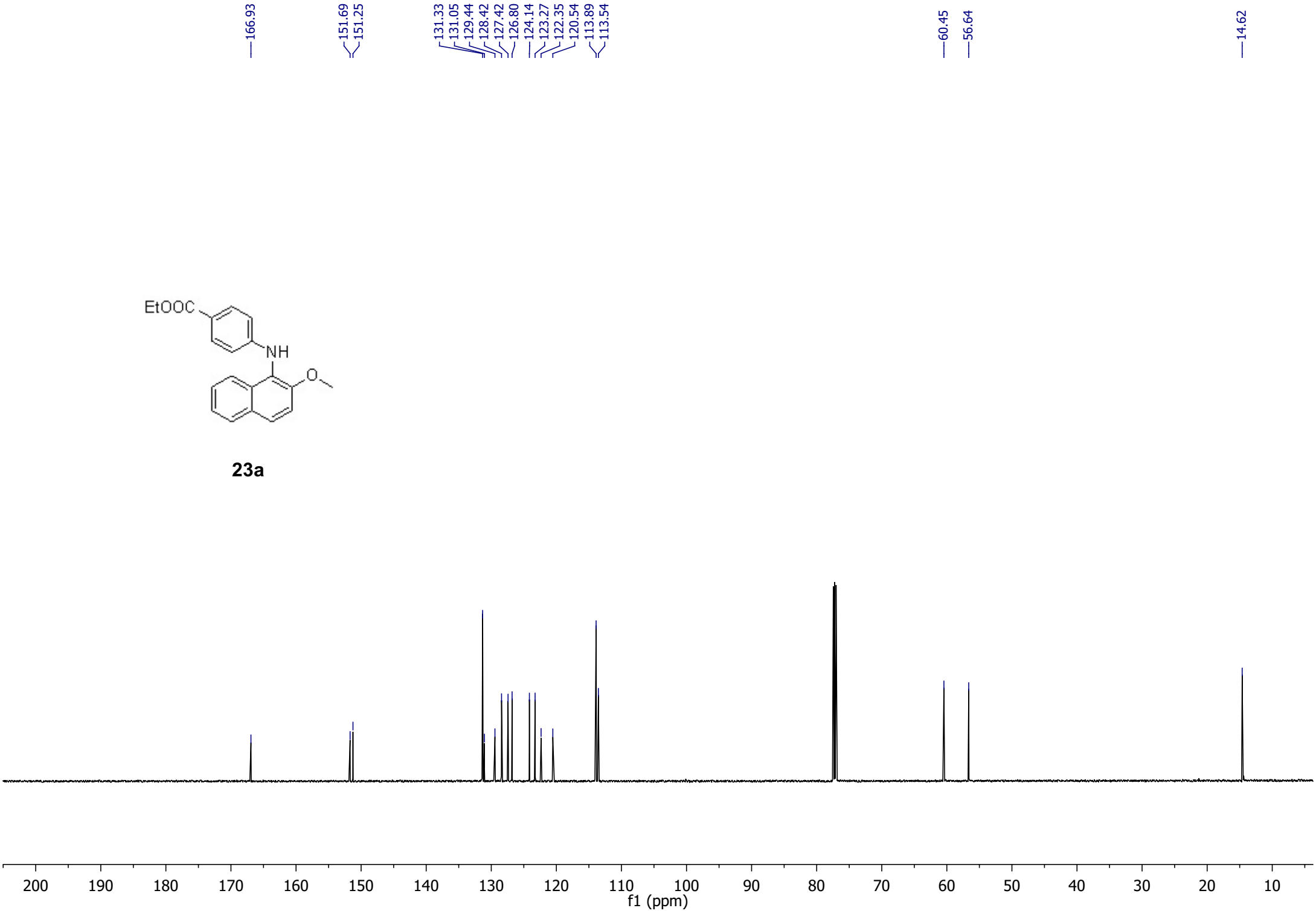

N
O
O

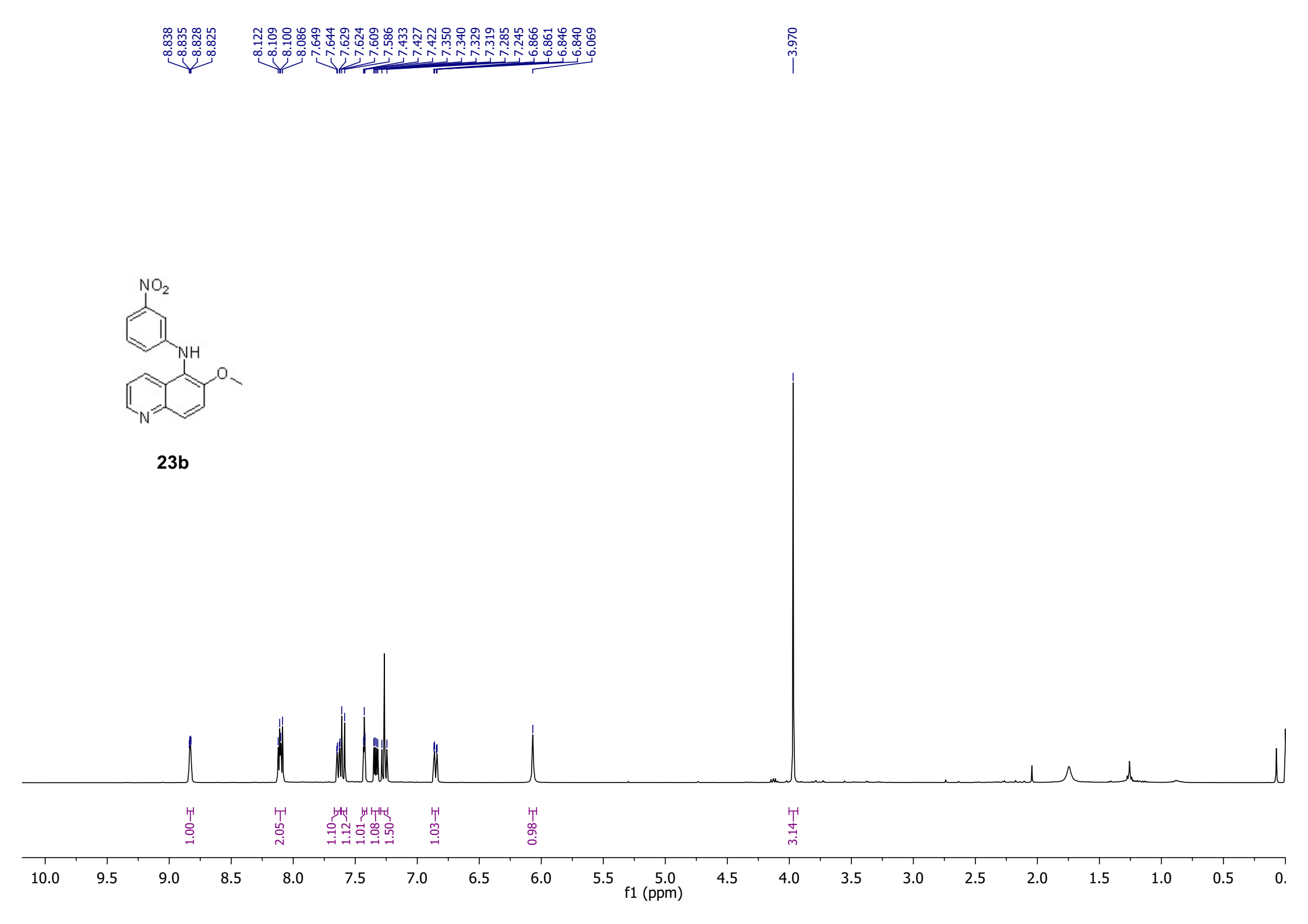
22

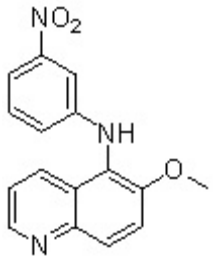
184.24
151.53
147.64
144.30
133.04
132.37
132.26
132.09
131.77
131.47
130.13
126.14
125.49
124.95
116.13
107.62
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.863
7.842
7.835
7.807
7.799
7.784
7.435
7.415
7.394
7.371
7.365
7.342
6.604
6.582
6.097
4.342
4.324
4.306
4.288
3.917
1.365
1.347
1.330
EtOOC
NH
O
2.97
1.95
2.99
2.00
0.90
1.96
2.99
3.07
f1 (ppm)

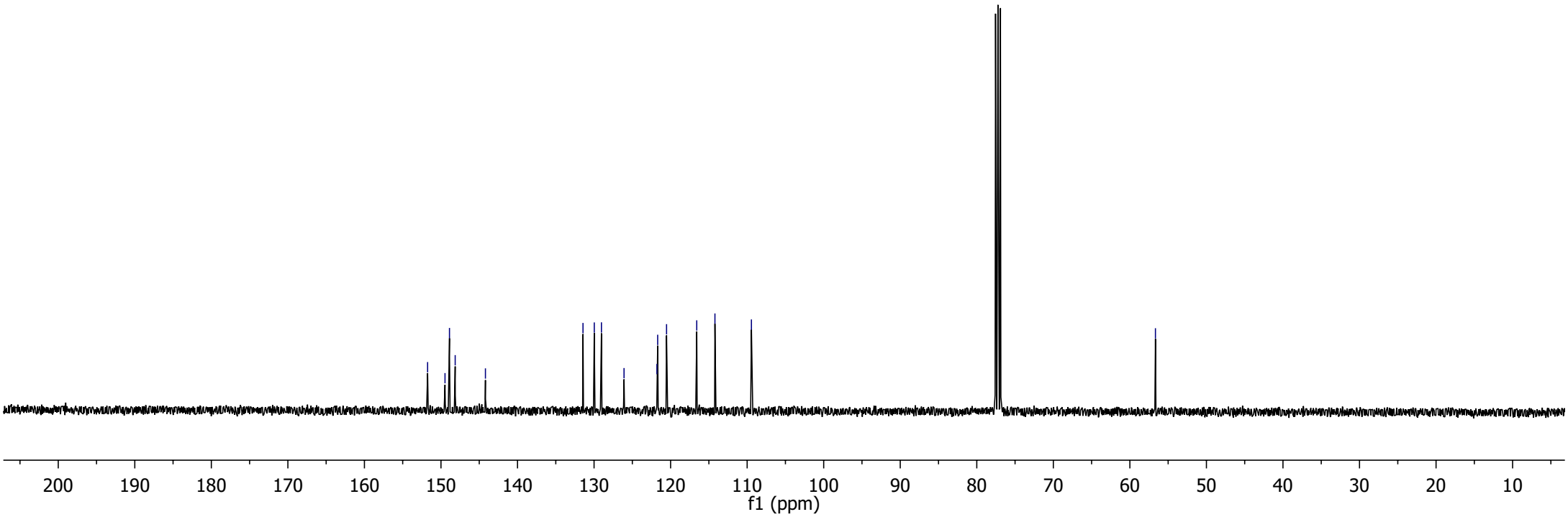
23a

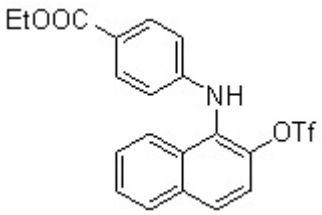

166.93
151.69
151.25
131.33
131.05
129.44
128.42
127.42
126.80
124.14
123.27
122.35
120.54
113.89
113.54
60.45
56.64
14.62
EtOOC
NH
O
23a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.838
8.835
8.828
8.825
8.122
8.109
8.100
8.086
7.649
7.644
7.629
7.624
7.609
7.586
7.433
7.427
7.422
7.350
7.340
7.329
7.319
7.285
7.245
6.866
6.861
6.846
6.840
6.069
3.970
NO2
NH
O
N
23b
1.00
2.05
1.10
1.12
1.01
1.08
1.50
1.03
0.98
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


NO2
NH
O
N

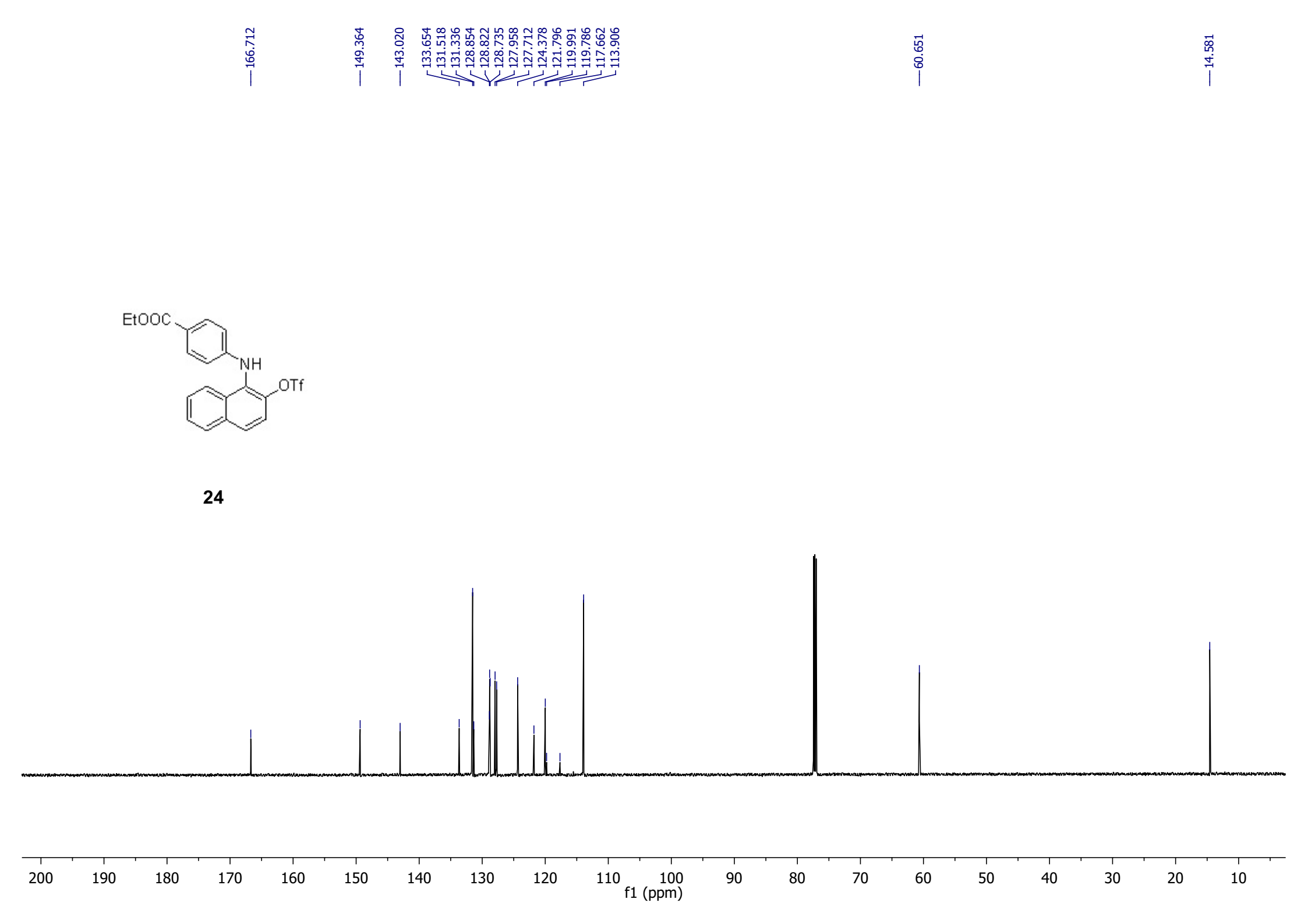
23b


151.75
149.47
148.89
148.14
144.19
131.45
129.97
129.04
126.08
121.79
121.69
120.53
116.59
114.21
109.44
56.66
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


EtOOC
NH
OTf

24

7.956
7.952
7.942
7.939
7.891
7.887
7.876
7.872
7.608
7.595
7.581
7.544
7.531
7.518
7.468
7.453
6.615
6.600
6.163
4.333
4.322
4.310
4.298
1.358
1.346
1.335
1.94
2.96
1.00
0.98
0.96
2.01
0.92
2.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.712
149.364
143.020
133.654
131.518
131.336
128.854
128.822
128.735
127.958
127.712
124.378
121.796
119.991
119.786
117.662
113.906
60.651
14.581
EtOOC
NH
OTf
24
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)